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(54) A METHOD FOR IMPROVING THE RELEASE OF A MOULDED CONCRETE BODY FROM THE  
MOULD

VERFAHREN ZUM LÖSEN EINES BETONGIESSTEILS VON DER FORM

PROCEDE D'AMELIORATION DU DEMOULAGE D'UN CORPS EN BETON

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• ACI JOURNAL, Feb. 1988, p.140, "Concrete  
Surface Finishes"

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## Description

The present invention relates to a method for improving the release of a moulded concrete body from the mould by applying an effective amount of a concrete release composition to the mould, said composition being an oil-in-water emulsion containing water in an amount of 10-90% by weight, an oily component in an amount of 10-90% by weight, one or more non-ionic surfactants in an amount of 0.5-20% by weight of the total emulsion, and one or more anionic surfactants provided as a sodium, potassium, lithium, ammonium or a lower alkylamine, lower alkyl-alkanolamine or lower alkanolamine salt of at the most 8 carbon atoms or a mixed salt, in which the amount of anionic surfactant in relation to the non-ionic surfactant is 1-100% by weight.

## BACKGROUND OF THE INVENTION

In order to allow the mould to be released from a moulded concrete body when said concrete body has been fully or partially set, it is necessary to apply a release composition to the mould before the moulding process, i.e. before the concrete composition is poured into the mould. The action of a concrete release agent is partly based on the principle that the curing of the concrete surface is delayed or even prevented so that the concrete body does not adhere to the surface of the mould. The delay in curing or the prevention of curing must only apply to a very thin layer of the concrete body so that the strength of the concrete body is not affected or is only affected to a minor extent.

Such compositions must fulfil various demands, i.e. they must be able to adhere to a certain amount to the mould, they must impart retarding influence to the surface layer of the concrete, they must have a suitable viscosity index so that they can be sprayed on the surface of the mould both in winter and in summer temperature conditions, and they should have a minimum hazardous effect on the environment.

Another way of obtaining a release ability is to apply a hydrophobic release composition so that the cured concrete will not adhere to the mould.

The release compositions used hitherto were normally based on mineral oils, and as additives were normally used kerosene in order to act as a viscosity decreasing agent, retarding agents for improving the release properties, and other additives which may be wetting agents, adhesives and corrosion-protective agents. Normally, known release compositions contain 65-99% by weight of mineral oil and kerosene and 1-35% by weight of additives. A preferred oil component is spindle oil having a viscosity of about 20 mm<sup>2</sup>/sec. (CSt) at 40°C. The kerosene used will normally have a boiling point of 150-200°C.

However, it is a well-known fact that the use of mineral oils involves a health risk causing toxic and allergic eczema, skin irritancy and skin cancer, and when used in sprayed form, the mineral oils may cause lung diseases. In addition to the health risks connected with the use of mineral oils *per se*, there is also an environmental disadvantage as mineral oils are normally only slightly bio-degradable. Therefore, the widespread use of mineral oils as concrete release agents involves a considerable risk of pollution.

It has been suggested to use vegetable oils to wholly or partially substitute mineral oils in concrete release agents. German Offenlegungsschrift No. 2,253,497 describes a mixture for use in demoulding concrete and plaster comprising a mineral oil and/or a hydrocarbon and at least one glyceride and additionally comprising a surfactant derived from a vegetable or animal fat. The use of surfactants permits the formation of a thin uniform film. The effect of glycerides is to form calcium salts or calcium-containing soaps which are only slightly soluble in water and prevent the curing of the concrete. However, glycerides are often too reactive (they have too strong a curing-preventing activity) to be used in mould release agents as it is difficult to modify their release properties. Hence, glycerides will often yield a porous surface layer caused by the prevention of curing in the outer layer. The use of glycerides is furthermore restricted by their high viscosity. Glycerides of higher saturated fatty acids are high-melting so that they will at normal temperatures separate from solutions based on mineral oils. So in spite of their harmlessness and their biodegradability, the use thereof is limited.

In order to impart low viscosity to release agents comprising mineral oils and/or vegetable oils, solvents were normally added. A suitable viscosity for applying mould release agents on moulds is in the range of  $\leq 35$  cP at 20°C.

Japanese Patent Application No. 50-97840 (Nippon Seikiyu K.K. and Mitsuo) discloses mixtures of free fatty acids and esters thereof which are used as retarding agents in release oils on a mineral oil basis. The oily agent (the fatty acids and esters) and the mineral oil are used in a weight ratio of 1:1-20, the oily agent containing a) 50-96% by weight of at least one component selected from C<sub>12-20</sub> saturated and C<sub>18-22</sub> unsaturated fatty acids and b) 50-4% by weight of at least one component selected from fatty acid esters of C<sub>12-20</sub> saturated and C<sub>18-22</sub> unsaturated fatty acids with C<sub>1-8</sub> monovalent alcohols. Hence, the retarding agent comprises at least 50% by weight of a mineral oil and at the most 25% by weight of a fatty acid ester.

In the Japanese application, it is described that combinations of certain fatty acids and certain esters in combination with a mineral oil, give an advantageous effect as a mould release agent. Specifically, the methyl ester of bovine fatty acid in admixture with a mineral oil is described as a comparison. However, methyl esters of fatty acids are in fact

characterized by their very strong retarding effect so that the esters, when added in only small amounts, increase the release effect of the mineral oil, but cannot substitute the mineral oil.

DE-A-29 25 485 discloses a release agent for concrete moulds comprising an aqueous dispersion of Montan wax which is a solid particulate material at ambient temperatures. Thus, the dispersion cannot form a continuous coating on mould surfaces. Another disadvantage is that the agent should be applied at elevated temperatures. Furthermore, the release effects are limited.

In contrast hereto, the present invention provides a mould release agent which is an oil-in-water emulsion which can be applied at ambient temperatures, forms a continuous coating on the surfaces and results in a homogeneous concrete surface.

## DESCRIPTION OF THE INVENTION

It has now been found that a mould release composition in the form of an oil-in-water emulsion containing water in an amount of 10-90% by weight of the total emulsion, an oily component in an amount of 10-90% by weight of the total emulsion, one or more non-ionic surfactants in an amount of 0.5-20% by weight of the total emulsion, and one or more anionic surfactants provided as a sodium, potassium, lithium, ammonium or a lower alkylamine, lower alkyl-alkanolamine or lower alkanolamine salt of at the most 8 carbon atoms or a mixed salt, in which the amount of the anionic surfactant in relation to the non-ionic surfactant is 1-100% by weight imparts excellent release properties to the mould and, furthermore, have several advantages compared to known mould release compositions.

When emulsions of oily substances are formed, three types of emulsions are possible, i.e. oil-in-water emulsions, water-in-oil emulsions and microemulsions (microemulsions are fine-disperse and translucent).

In order that the release composition should bind efficiently to the mould, it would be advantageous if the water were incorporated into the oil so as to form a water-in-oil emulsion. However, the usefulness of such emulsions is limited by the fact that the application of the emulsion on the mould is extremely difficult. The viscosity of the emulsion will increase along with the increase in the amount of the emulsified water, and therefore, the applied amount will increase. At the same time, there will be a tendency for the emulsion to become less viscous after the spreading as the water evaporates, and thus, it will have a tendency to run off from inclined and vertical surfaces. Release oils which are formulated as water-in-oil emulsions will therefore have a limited usefulness.

Oil-in-water emulsions may be prepared as low-viscous compositions. However, they usually have a poor adhesion to the mould so that they are torn off at the filling up with concrete. It has now surprisingly been found that oil-in-water emulsions may be prepared in such a way that after application on the mould, the emulsion gradually changes its structure so as to be converted into an oily film or a water-in-oil emulsion as the water evaporates. Then the emulsion adheres strongly to the mould so that the emulsion in a dosage of 10-100 g/m<sup>2</sup>, preferably 15-70 g/m<sup>2</sup>, and especially 20-50 g/m<sup>2</sup>, after a drying period of 2-20 minutes, depending on the temperature, and at a relative humidity of about 40-70%, is converted into an adhering oily film or emulsion of the water-in-oil type which will not easily be washed off when rinsing with water or rubbed off at the filling up with the concrete mixture.

When the emulsion has been converted, it will be reasonably resistant to rain, which is an important feature when moulding outdoors.

As the oily component in the emulsion it is possible to use a mineral oil or a mixture of more mineral oils; a triglyceride with 10-24 carbon atoms in each fatty acid moiety, optionally in admixture with a mineral oil; one or more esters of an aliphatic carboxylic acid with a mono- or dihydric alcohol, having melting points below 35°C, preferably below 25°C and especially below 15°C, the total number of carbon atoms in the esters being 8-46, especially 10-38, preferably 12-30; a mixture of mineral oil(s) and esters as mentioned above, optionally also comprising a triglyceride with 10-24 carbon atoms in each fatty acid moiety, in which the content of ester is 1-100%, especially 10-100%, and preferably 35-100%.

The esters to be used as oily component in the concrete release compositions are defined in detail below.

Emulsions formulated with a mixture of esters as defined above and mineral oil will generally be more stable when the emulsified oily phase consists of a mixture of mineral oil and ester as defined above in the mixing ratio of from 1:2 to 2:1, by weight.

The oily phase in the emulsion may also consist of mixtures of triglycerides with 10-24 carbon atoms in each fatty acid moiety and/or mineral oil and/or one or more esters as defined above and below. Chlorinated oils, polyglycols, C<sub>10</sub>-20 fatty alcohols and other oily components may be used as further oily components.

Examples of triglycerides with 10-24 carbon atoms in each fatty acid moiety are vegetable oils and marine oils.

When the oily component is a mineral oil, it is preferred that this oil comprises at the most 9% of aromatics, more preferred at the most 5% and especially at the most 2% of aromatics, as the contents of aromatics, because of their toxicity, should be kept as low as possible. Preferred mineral oils have a boiling point of at least 250°C.

If the oily component is a mixture of mineral oil(s) and a vegetable oil or marine oil, a preferred ratio between mineral oil and vegetable oil or marine oil is from 99 : 1 to 50 : 50.

It is preferred that the content of oily component in the emulsion is 15-75%, preferably 25-55%, by weight of the total emulsion.

The oil-in-water emulsion may be prepared by mixing common tap water in an amount of 10-90% by weight, preferably 20-80% by weight and especially 30-65% by weight, with an oily component as defined above in an amount of 10-90% by weight, preferably 15-75% by weight and especially 25-55% by weight, of the whole mixture, a surfactant mixture consisting of one or more non-ionic surfactants which are selected from the group consisting of ethoxylated, propoxylated and co-ethoxylated/propoxylated surfactants with a Hypophil-Lipophil Balance corresponding to an HLB value of between 5.0 and 11, preferably between 5.5 and 9.9 and especially between 6.0 and 9, in an amount of 0.5-20% by weight of the whole mixture, preferably 1-12% by weight and especially 2-7% by weight, and one or more anionic surfactants as salts as defined above, the amount of the anionic surfactant being 1-100%, calculated in relation to the amount of the non-ionic detergent on a weight basis, preferably 2-50% and especially 4-25%, and optionally additives such as antifreezes, corrosion inhibitors, further concrete retarding agents, stabilizers, and hydrophobicity-imparting agents such as polyvalent metal salts of C<sub>10-22</sub> alkyl carboxylic acids, etc. (HLB = Hydrophil-Lipophil-Balance; HLB values are theoretical, calculated values used in connection with ethoxylated non-ionic detergents. The HLB is directly proportional with the contents of polyethylene oxide. HLB values are between 0 and 20; a low HLB indicates an oil-soluble surfactant, and the water-solubility increases with increasing HLB values).

Examples of preferred non-ionic surfactants are ethoxylated C<sub>4-15</sub> alkyl or di-C<sub>4-15</sub> alkyl phenols such as ethoxylated octyl or nonyl phenol and ethoxylated dioctyl or dinonyl phenol, ethoxylated C<sub>8-22</sub> fatty alcohol and polyethylene glycol esters of C<sub>10-22</sub> fatty acid, all having HLB values as stated above.

The anionic surfactants are provided as a sodium, potassium, lithium, ammonium or a lower amine or alkanolamine salt containing not more than 8 carbon atoms and preferably at the most 6 carbon atoms (e.g. a monoethanolammonium or a mono- or dialkylethanolammonium salt) or a mixed salt of compounds as mentioned below.

Examples of preferred anionic surfactants are salts of mono- and diphosphoric acid esters of ethoxylated C<sub>4-15</sub> alkyl and di-C<sub>2-15</sub> alkyl phenols and ethoxylated fatty C<sub>8-22</sub> alcohols. Salts of C<sub>8-22</sub> alkylsarcosines, C<sub>1-15</sub> alkylphenylcarboxylic acids, arylcarboxylic acids, aryl-C<sub>1-15</sub> alkylcarboxylic acids, C<sub>1-15</sub> alkylaryl-C<sub>1-15</sub> alkylcarboxylic acids, phenoxy-C<sub>1-15</sub> alkylcarboxylic acids, C<sub>1-15</sub> alkylphenoxy-C<sub>1-15</sub> alkylcarboxylic acids, C<sub>8-30</sub> alkylcarboxylic acids and the corresponding dicarboxylic acids and the corresponding unsaturated analogues thereof are also useful. Other useful acid salts are salts of dimerised or trimerised unsaturated fatty acids. Especially useful are salts of C<sub>10-30</sub> fatty acids such as oleic acid, lauric acid, myristic acid, palmitic acid and stearic acid. Salts of saturated acids are especially preferred as they give the most homogeneous concrete surface and of these, salts of stearic acid gives very stable emulsions. Hence, especially preferred anionic surfactants are salts of stearic acid such as sodium and ammonium stearate. Salts of the acids mentioned above may be formed by neutralizing the acids in the emulsions.

It is advantageous that the anionic surfactant is provided as an ammonium or a volatile amine salt as, simultaneously with the evaporation of water, release of ammonia or volatile amine will take place so that the emulsion will be converted into a water-in-oil emulsion more quickly. However, it is no prerequisite that a conversion of the salt into acid takes place; thus, compositions may be formed in which the anionic surfactant is present as a sodium salt and in which the mould release agent adheres so strongly to the mould that it is not torn off during the moulding process. It is not a prerequisite that the emulsion has been converted into a water-in-oil emulsion before the filling up with concrete. Concrete is highly alkaline and contain a saturated solution of calcium hydroxide. When this solution comes into contact with the anionic surfactant, the latter will be converted into a calcium salt which is more hydrophobic so that the mould release agent is attached more strongly to the mould.

It is an important feature of the invention that the surfactant mixture comprises a non-ionic surfactant in a large amount, i.e. 0.5-20% by weight of the total emulsion, e.g. about 5% by weight, in combination with an anionic surfactant in a minor amount, i.e. 0.05-6% by weight of the total emulsion, e.g. about 0.5-1%, such as 0.7%, by weight. The non-ionic surfactant has a stabilizing effect on the emulsion.

It is a well-known fact that an adhering oily film can be prepared from an ammonium salt of a fatty acid, the film being formed when the ammonia part of the salt is liberated and the salt is converted into a free fatty acid. Hence, it was to be expected that anionic surfactants in the form of ammonium and amine salts as defined above should be used in large amounts. The use of large amounts of ammonium salts and the resulting liberation of ammonia to the environment would be disadvantageous. It is an important aspect of the invention that the use of anionic surfactants in the form of salts as defined above in combination with large amounts of non-ionic surfactants lead to stable emulsions which shortly after the application to surfaces are converted into adhering oily films or water-in-oil emulsions.

The pH of the emulsion is very decisive for the emulsion stability, the corrosion stability and the skin tolerance. A pH of the solution for use of 7.4-10.5, preferably 7.8-10 and especially 8.2-9.5 should be preferred.

The quality of the water used is also very important for both the emulsion stability and its tendency to cause rust when sprayed onto metal moulds. The use of deionized water cause the fewest corrosion problems, but the tendency to corrosion especially depends on the surfactants used. In order to obtain a satisfactory long-term stability of the emulsion formed, it is advantageous to use water of a certain hardness. Thus, the best emulsion stability is obtained when

using water with a hardness of 2-75 ° d water, preferably 3-50 ° d and especially 5-40 ° d (the ° d of the water denotes the total amount of Ca + Mg, expressed as the equivalent amount of CaO, 1 ° d corresponds to 10 mg of CaO).

The emulsion may be prepared by the manufacturer or it may be prepared by the user immediately prior to use by diluting an oily concentrate to the desired concentration, e.g. by diluting with two parts of water.

5 In case the product is prepared as a product ready for use, it is important that the emulsion is long-term stable and that the resistance to cold is good.

One aspect of the invention relates to a method for improving the release of a moulded concrete body from the mould by applying an effective amount of an oil-in-water emulsion prepared by addition of water to an emulsion concentrate comprising the constituents of the emulsion defined above, but without the content of water. Special emulsions are  
10 emulsions which after application on a surface are converted into an adhering oily film or water-in-oil emulsion which will not be easily washed off when rinsing the surface with water.

An oil-in-water emulsion as defined above to be used for improving the release of a moulded concrete body from the mould, is prepared by a method in which one or more non-ionic surfactants is/are dissolved in the oily phase, and said oily phase is added to the aqueous phase in which one or more anionic and optionally one or more cationic surfactants are dissolved or dispersed, said aqueous phase being, if necessary, pH adjusted, and the addition of the oily  
15 phase to the aqueous phase being carried out with vigorous stirring.

In order to obtain a stable emulsion, the mixture of the oily and the aqueous phases with their contents of auxiliary agents may be subjected to an emulsification process in an apparatus conventionally used as emulsifier, i.e. the mixture may be subjected to an intensive mechanical processing in which it passes through a slit in which it is influenced by  
20 high shear forces. Such a slit opening should be at the most 10 mm, preferably at the most 3 mm, more preferably at the most 1 mm, and especially at the most 0.2 mm. Examples of apparatuses which may be used are homogenizers, pin disc mills, high-speed mixers of the Silverson type in which the movable part is placed in a stationary cylinder, and high-pressure homogenizers.

In order to secure the resistance to cold, glycols and/or lower polyglycols and/or glycol ethers such as glycerol, propylene glycol, ethylene glycol, butylglycol, propylene glycol methylether, cellosolve and diethylene glycol may be added  
25 to the mixture. Because of their good skin acceptance, especially glycerol and propylene glycol are preferred. Moreover, the two substances in a total amount of 1-20%, especially in amounts of 5-10%, calculated on a weight basis of the finished emulsion, have a positive effect on the emulsion stability.

Heavy demands are made to the exact adjustment of the described emulsion systems. If the release oil emulsion  
30 is to be sold as a finished emulsion, which is preferable, both the emulsion stability during a period of about 3-6 months and the tendency of the emulsion to be converted into a water-in-oil emulsion after spraying onto the mould should be optimized. Heavy selection demands are made to both the single components and to the adjustment of the amounts used.

The finished long-term durable oil-in-water release oil emulsion which after drying forms an oily film or water-in-oil  
35 emulsion which cannot easily be washed off with water may thus be prepared by mixing water of a suitable hardness in an amount of 10-90% by weight of the total composition, preferably 20-80% by weight and especially 30-65% by weight, one or more of the oily components described above in an amount of 10-90% by weight, preferably 15-75% by weight and especially 25-55% by weight, a surfactant mixture of one or more ethoxylated non-ionic surfactants with a HLB value between 5.0 and 10.5, preferably between 5.5 and 9.9 and especially between 6.0 and 9, in an amount of 0.5-  
40 20% by weight, preferably 1-12% by weight and especially 2-7% by weight, and one or more anionic surfactants which may be provided as a sodium, potassium, lithium, ammonium or a lower amine or alkanolamine salt containing not more than 8 carbon atoms and preferably at the most 6 carbon atoms or a mixed salt thereof, the amount of the anionic detergent being 0.05-4% by weight of the total emulsion, preferably 0.1-4%, more preferably 0.15-2% and especially 0.2-1%. As a further stabilizer and additive for the resistance to cold, the release oil emulsion may contain 1-20%, preferably 2-  
45 15% and especially 5-10% by weight of a glycol and/or a lower polyglycol and/or a glycol ether. The pH of the emulsion should be 7.4-10.5, preferably 7.8-10, and more preferably 8.2-9.5.

In a preferred aspect of the invention, the oily component in the oil-in-water emulsion is an ester of an aliphatic carboxylic acid with a mono- or dihydric alcohol, the total number of carbon atoms in the ester being 8-46, especially 10-38, preferably 12-30, and having a melting point of at the most 35°C, preferably 25°C, more preferably 15°C.

It is advantageous to use esters of aliphatic carboxylic acids as defined below with melting points of at the most  
50 35°C, preferably 25°C, and especially 15°C, in concrete release compositions, both in emulsified and in non-emulsified form, as the esters of aliphatic carboxylic acids are much more bio-degradable and less toxic than mineral oils; it is possible to modify the extent of release from the mould to fit the desired rate of retardation of the concrete; the esters are less viscous than the mineral oils normally used, and their viscosity index is more suitable, i.e. many esters have viscosity indexes in the range of 120-150, which is especially advantageous when the esters are used in non-emulsified  
55 form.

Therefore, it is normally not necessary to add viscosity-decreasing agents when the esters are used in the non-emulsified form, and an environmental hazard is thus removed.

The alcohol moiety of the ester may be derived from a monoalcohol of the formula I or II



in which  $R_1$  and  $R_2$  are each a straight or branched, saturated or unsaturated hydrocarbyl group of 1-22 carbon atoms, and  $R_3$  is a straight or branched, saturated or unsaturated hydrocarbylene chain of 2-22 carbon atoms, and the total number of carbon atoms in  $R_2$  and  $R_3$  being at the most 24. It is preferred that the hydrocarbyl groups  $R_1$  and  $R_2$  each have 2-20 carbon atoms, especially 2-12 and more preferably 6-9 carbon atoms, and that  $R_3$  is a straight or branched saturated hydrocarbylene chain of 2-9 carbon atoms.

As examples of alcohols of the formulae I and II may be mentioned methanol, ethanol, propanol, isopropanol, butanol, isobutanol, amyl alcohol, hexyl alcohol, heptyl alcohol, isoheptyl alcohol, octyl alcohol, isooctyl alcohol, 2-ethyl-hexyl alcohol, nonyl alcohol, cetyl alcohol, isocetyl alcohol, ethoxyethanol, butoxyethanol, and unsaturated analogues thereof. Preferred alcohols are isopropanol, isobutanol, octyl alcohol, isooctyl alcohol, 2-ethyl-hexyl alcohol and nonyl alcohol.

The acid moiety in the esters may be derived from an aliphatic monocarboxylic acid of the formula  $R_4COOH$  in which  $R_4$  is a straight or branched, saturated or unsaturated hydrocarbyl group of 1-30 carbon atoms, preferably 8-20 carbon atoms, and optionally substituted by one or more hydroxy groups, the acid moiety preferably being derived from a saturated carboxylic acid. Examples of such acids are butanoic acid, hexanoic acid, octanoic acid, decanoic acid, 2-ethylhexanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid and hydroxy-substituted stearic acid. Furthermore, mixtures of technical fatty acids such as  $C_{16}$  and  $C_{18}$  fatty acids may be used.

A preferred class of esters to be used according to the invention consists of esters selected from the group consisting of 2-ethyl-hexyl laurate, 2-ethyl-hexyl myristate, 2-ethyl-hexyl palmitate, 2-ethyl-hexyl stearate, isobutyl stearate, isopropyl myristate, isooctyl esters of  $C_{16}$  and  $C_{18}$  technical fatty acids, and mixtures thereof.

Another preferred class of acid moieties is derived from unsaturated acids such as oleic acid, or ricinoleic acid, e.g. 2-ethyl-hexyl oleate and isobutyl oleate.

Especially suitable esters are  $C_{2-20}$  monoalcohol esters of oleic acid,  $C_{2-12}$  monoalcohol esters of lauric and myristic acids and  $C_{6-9}$  monoalcohol esters of palmitic and stearic acids.

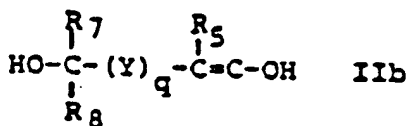
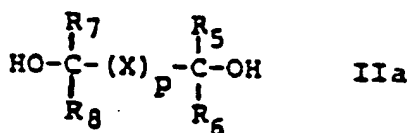
The acid moiety of the ester may be derived from an acid of the general formula  $HOOC-(A)_m-COOH$  in which A is a straight or branched, saturated or unsaturated hydrocarbylene chain of 2-16 carbon atoms which is optionally substituted by one or more hydroxy groups, and m is 0 or 1.

Examples of dicarboxylic acids are oxalic acid, succinic acid, 2-hydroxy succinic acid, 2,3-dimethyl succinic acid, glutaric acid, adipic acid, pimelic acid, hexanedicarboxylic acid, azelaic acid, and sebacic acid, said acids being esterified on one or both of the acid groups.

It is preferred that the ester component in the concrete release composition both in emulsified and in non-emulsified form is a mixture of at least two esters selected from the group consisting of diisobutyl succinate, diisopropyl adipate, di(ethyl-hexyl) succinate, di(ethyl-hexyl) adipate, and mono(ethyl-hexyl) adipate, optionally in admixture with 2-ethyl-hexyl stearate or 2-ethyl-hexyl palmitate. These esters are preferred because of their viscosity which makes them especially suitable as mould release agents in non-emulsified form. Furthermore, they are inexpensive.

A suitable ester may also be derived from an acid of the formula  $HOOC-A'-COOH$  in which  $A'$  is a unsaturated hydrocarbylene chain of 2-6 carbon atoms.

Further examples of esters in the mould release compositions to be used in the methods according to the invention are esters wherein the alcohol moiety is derived from a dialcohol of the formula IIa or IIb



wherein  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  may be the same or different and each designates hydrogen, straight or branched alkyl or straight or branched unsaturated hydrocarbyl chain,  $p$  is 0 or 1,  $q$  is 0 or 1,  $X$  is a straight or branched saturated or unsaturated hydrocarbylene chain of 1-15 carbon atoms, and  $Y$  is a straight or branched saturated or unsaturated hydrocarbylene chain of 1-15 carbon atoms, the total number of carbon atoms in the dialcohol molecules being at the most 18, preferably at the most 12.

A preferred class of esters of the above-mentioned class are esters wherein the alcohol moiety is derived from alcohols selected from the group consisting of ethylene glycol, propylene glycol, hexylene glycol, dimethyl propanediol, and 2,2,4-trimethylene pentane(-1,3)-diol.

The acid moiety of esters in which the alcohol moiety is derived from a dialcohol of the formula IIa or IIb is derived from an acid of the formula  $R_9\text{COOH}$  wherein  $R_9$  is a straight or branched, saturated or unsaturated hydrocarbyl group of 1-22 carbon atoms which is optionally substituted by one or more hydroxy groups, and said acid is preferably selected from the group consisting of formic acid, acetic acid, propionic acid, isopropionic acid, butyric acid, isobutyric acid, lactic acid, pentanoic acid, hexanoic acid, isoheptanoic acid, octanoic acid, isooctanoic acid, 2-ethylhexanoic acid, nonanoic acid and decanoic acid, and mixtures of technical  $C_{16}$  and  $C_{18}$  fatty acids.

Hence, preferred esters to be used in the methods according to the invention are selected from the group consisting of ethyleneglycol diisobutyrate, propyleneglycol diisobutyrate, hexyleneglycol monoisobutyrate, hexyleneglycol diisobutyrate, dimethylpropanediol monoisobutyrate, dimethylpropanediol diisobutyrate, 2,2,4-trimethylpentane-(1,3)-diol monoisobutyrate and 2,2,4-trimethylpentane-(1,3)-diol diisobutyrate.

Examples of esters are: hexyl acetate, 2-ethylhexyl acetate, octyl acetate, isooctyl acetate, cetyl acetate, dodecyl acetate, tridecyl acetate; butyl butyrate, isobutyl butyrate, amyl isobutyrate, hexyl butyrate, heptyl butyrate, isoheptyl butyrate, octyl butyrate, isooctyl butyrate, 2-ethylhexyl butyrate, nonyl butyrate, isononyl butyrate, cetyl butyrate, isocetyl butyrate;

ethyl hexanoate, propyl hexanoate, isopropyl hexanoate, butyl hexanoate, isobutyl hexanoate, amyl hexanoate, hexyl hexanoate, heptyl hexanoate, isoheptyl hexanoate, octyl hexanoate, 2-ethylhexyl hexanoate, nonyl hexanoate, isononyl hexanoate, cetyl hexanoate, isocetyl hexanoate;

methyl octanoate, ethyl octanoate, propyl octanoate, isopropyl octanoate, butyl octanoate, isobutyl octanoate, amyl octanoate, hexyl octanoate, heptyl octanoate, isoheptyl octanoate, octyl octanoate, isooctyl octanoate, 2-ethylhexyl octanoate, nonyl octanoate, isononyl octanoate, cetyl octanoate, isocetyl octanoate;

methyl 2-ethylhexanoate, ethyl 2-ethylhexanoate, propyl 2-ethylhexanoate, isopropyl 2-ethylhexanoate, butyl 2-ethylhexanoate, isobutyl 2-ethylhexanoate, isoamyl 2-ethylhexanoate, hexyl 2-ethylhexanoate, heptyl 2-ethylhexanoate, isoheptyl 2-ethylhexanoate, octyl 2-ethylhexanoate, isooctyl 2-ethylhexanoate, 2-ethylhexyl 2-ethylhexanoate, nonyl 2-ethylhexanoate, isononyl 2-ethylhexanoate, cetyl 2-ethylhexanoate, isocetyl 2-ethylhexanoate;

methyl decanoate, ethyl decanoate, propyl decanoate, isopropyl decanoate, butyl decanoate, isobutyl decanoate, isoamyl decanoate, hexyl decanoate, heptyl decanoate, isoheptyl decanoate, octyl decanoate, isooctyl decanoate, 2-ethylhexyl decanoate, nonyl decanoate, isononyl decanoate, cetyl decanoate, isocetyl decanoate;

methyl laurate, ethyl laurate, propyl laurate, isopropyl laurate, butyl laurate, isobutyl laurate, isoamyl laurate, hexyl laurate, heptyl laurate, isoheptyl laurate, octyl laurate, isooctyl laurate, 2-ethylhexyl laurate, nonyl laurate, isononyl laurate, cetyl laurate, isocetyl laurate;

ethyl oleate, propyl oleate, isopropyl oleate, butyl oleate, isobutyl oleate, isoamyl oleate, hexyl oleate, heptyl oleate, isoheptyl oleate, octyl oleate, isooctyl oleate, 2-ethylhexyl oleate, nonyl oleate, isononyl oleate, cetyl oleate, isocetyl oleate;

diethyl succinate, dipropyl succinate, diisopropyl succinate, dibutyl succinate, diisobutyl succinate, diisoamyl succinate, dihexyl succinate, diheptyl succinate, diisoheptyl succinate, dioctyl succinate, diisooctyl succinate, di-2-ethylhexyl succinate, dinonyl succinate, diisononyl succinate, dicetyl succinate, diisocetyl succinate;

dimethyl adipate, diethyl adipate, dipropyl adipate, diisopropyl adipate, dibutyl adipate, diisobutyl adipate, diisoamyl adipate, dihexyl adipate, diheptyl adipate, diisoheptyl adipate, dioctyl adipate, diisooctyl adipate, di-2-ethylhexyl adipate, dinonyl adipate, diisononyl adipate, dicetyl adipate, diisocetyl adipate;

isopropyl myristate, isobutyl myristate, butyl myristate, amyl myristate, hexyl myristate, heptyl myristate, isoheptyl myristate, octyl myristate, 2-ethylhexyl myristate, nonyl myristate, isononyl myristate, cetyl myristate, isocetyl myristate;

isopropyl palmitate, isobutyl palmitate, butyl palmitate, amyl palmitate, hexyl palmitate, heptyl palmitate, isoheptyl palmitate, octyl palmitate, 2-ethylhexyl palmitate, nonyl palmitate, isononyl palmitate, cetyl palmitate, isocetyl palmitate; isopropyl stearate, isobutyl stearate, butyl stearate, amyl stearate, hexyl stearate, heptyl stearate, isoheptyl stearate, octyl stearate, 2-ethylhexyl stearate, nonyl stearate, isononyl stearate, cetyl stearate, isocetyl stearate.

The rate of retardation may be varied by varying the ester composition. In general, if short-chained alcohols are used in the esters, the esters will act more retarding; tests have shown that methyl oleate has a retarding effect in the same range as vegetable oils; in some application areas, such as in the production of concrete articles where the character of the surface is of less importance, a certain retarding effect is desired, as a good release activity is ensured.

If the acid moiety of the ester has a high level of double and triple bonds such as in tall oil (containing both linolic

and linoleic acids), the retarding effect will be large even if the alcohol moiety is derived from a long-chained alcohol. Hence, esters of tall oil can be used when the retarding effect is to be increased. Calcium salts of linolic and linoleic acids are sticky. Vegetable oils which always contain linolic and linoleic acids yield eaters which may give the concrete surface a botched appearance when used alone in release compositions.

Owing to their hydrophobic properties the synthetic esters are in general able to ensure an advantageous release effect without having a decisive retarding effect on the surface of the concrete body, thus imparting an attractive surface to the concrete body. These properties could also be achieved by using mineral oil products, but not, or only with difficulties, by using vegetable oils. However, mineral oil products are normally not biodegradable as are the synthetic esters used according to the invention. Normally the mould release agent is rinsed off the mould after use by means of water which is conducted to the environment or the moulds are brushed off and the dust conducted to the environment. Therefore, the use of biodegradable synthetic esters gives less or no poisoning of the environment.

The liquid mould release compositions may be applied to the surface of the mould, e.g. by spraying with a normal spraying device such as a hand sprayer, or by means of compressed air, or by means of a brush. The compositions are used in an amount of 10-100, especially 15-70, and preferably 20-50, g/m<sup>2</sup> surface of the mould.

Many laboratory tests have shown that the mould release compositions comprising esters in emulsion form described above may give highly satisfactory test results for long periods of time, but that they may then suddenly fail as the release effect decreases and concrete residues which are difficult to wash off are left behind. This has also been observed in practical tests. The reason may be that the esters are not 100% stable and that, during the concrete curing process, they are to a limited degree saponified (decomposed) to free fatty acids which will act in a limited retarding way on the concrete and thus promote the release effect. If the curing takes place slowly, the saponification process (the decomposition of the ester) be very limited so that it becomes more difficult for the cured concrete to be released from the mould. Most moulding tests have been carried out in a way so that the demoulding occurs after 24 hours. It has been found that the release problems become bigger if the curing is complete already after 16-17 hours.

A number of screening tests have shown the following tendencies:

1) glycerol may act slightly adhesive and thus bind the concrete to the mould, which means that the use of glycerol is limited,

2) the ethoxylated non-ionic surfactant may also act slightly adhesive and the tendency is the weakest if the degree of ethoxylation is as small as possible,

3) addition of surfactants with cationic groups containing an amino group or another group comprising a quaternary N-atom and with at least 10 carbon atoms in the hydrophobic part of the molecule in combination with the anionic detergents mentioned above will lead to emulsions which to a still higher degree will stick to the concrete mould. The cationic surfactant should be employed in amounts of 5-100%, calculated on a molar basis of the anionic surfactant, preferably 10-80% and especially 20-60%. When the emulsion binds optimally to the mould so that it is distributed in a layer with homogeneous thickness, it will be more active and thus promote the release effect. Examples of suitable surfactants are mono-, di- and trivalent amines, ethoxylated amines, quaternary ammonium compounds, ampholytes (amphoteric compounds containing at least one amine group and at least one acid group). A suitable ampholyte is coco alkyl  $\beta$ -amino propionic acid. Examples of especially suitable cationic surfactants are imidazoline derivatives such as 1-(2-hydroxyethyl)-2-C<sub>8-22</sub>-alkyl- and -C<sub>8-22</sub>-alkenyl-2-imidazoline, e.g. imidazoline 0 (1-(2-hydroxyethyl)-2-heptadecenyl-2-imidazoline),

4) retarding agents which release carboxylic acids or hydroxycarboxylic acids will also improve the release effect. Monoglycerides of C<sub>2-24</sub> fatty acids which are fully or partially acylated with a C<sub>1-4</sub> organic acid are especially suitable. Diacetylated monoglycerides are used in the food industry and are characterized by being low-viscous liquids at normal temperature, also if the fatty acid moiety is saturated. Monoglycerides and diacetylated monoglycerides of C<sub>8-24</sub> fatty acids may be so selected that they efficiently stabilize the release oil emulsion simultaneously with reducing the content of the ethoxylated and/or propoxylated and/or co-ethoxylated/propoxylated non-ionic surfactant. The glyceride derivatives mentioned above may be so selected that the content of the long-chain carboxylic acids is preferably saturated. This ensures that the concrete retardation occurs without the concrete surface becoming stained.

Mono- or di-C<sub>1-4</sub> acylated monoglycerides of C<sub>2-24</sub> fatty acids which optionally bear a hydroxy group, give a retarding effect on concrete release agents, which means that they can be used as concrete release agents in non-emulsified form together with mineral oil(s) and/or esters of the type defined above. The monoglycerides are preferably mono- or diacetylated or mono- or diformylated. The fatty acid may be saturated or unsaturated.

Long-term stable oil-in-water release oil emulsions which are stable at normal storage for at least 3-6 months with good release properties and in which the single components can be adjusted to the effect that the emulsion in a dosage on the concrete mould of 10-100 g/m<sup>2</sup>, preferably 15-70 g/m<sup>2</sup> and especially 20-50 g/m<sup>2</sup> after a drying period of 2-20 minutes at ambient temperature above the freezing point, e.g. at about 20°C, and at a relative humidity of about 40-70%



is converted into an attached film which cannot immediately be washed off with water or at the filling-up be rubbed off by the concrete mixture. Such an emulsion may be prepared by mixing water of a suitable hardness in an amount of 10-90% by weight of the total composition, preferably 20-80% and especially 30-65%, and an oily component as defined above in an amount of 10-90% by weight, preferably 15-75% and especially 25-55%, to which has been added a non-ionic surfactant component comprising a mono- or di- $C_{1-4}$ -acylated, preferably mono- or diacetylated, monoglyceride of a saturated or unsaturated  $C_{2-24}$  fatty acid, preferably a  $C_{8-24}$  fatty acid which may optionally bear a hydroxy group and optionally one or more ethoxylated, propoxylated and/or coethoxylated/propoxylated non-ionic surfactants with a HLB value of between 5.0 and 10.5, preferably between 5.5 and 9.9 and especially between 6.0 and 9, and/or one or more monoglycerides of saturated or unsaturated  $C_{8-24}$  fatty acids which may optionally bear a hydroxy group. The non-ionic surfactant component may also comprise at least one member of the group consisting of ethoxylated, propoxylated and/or co-ethoxylated/propoxylated surfactants with an HLB value of 5-10.5, preferably 5.5-9.9, and especially 6-9, monoglycerides of saturated and unsaturated  $C_{8-24}$  fatty acids, optionally bearing a hydroxy group, and mono- or di- $(C_{1-4})$ -acylated monoglycerides of  $C_{2-24}$  fatty acids, optionally bearing a hydroxy group. The non-ionic surfactant component is used in an amount of 0.5-20% by weight of the total emulsion, preferably 1-12% and especially 2-7%. Furthermore, the emulsion should contain a composition of ionic (anionic/cationic mixture) surfactants comprising at least one anionic surfactant which may be provided as a sodium, potassium, lithium, ammonium or a lower amine or alkanolamine salt containing at the most 8 carbon atoms, preferably at the most 6 carbon atoms, in the alkyl and alkanol moiety, or a mixed salt thereof. The amount of the anionic part of the ionic surfactant composition should preferably be 0.05-6% by weight of the total emulsion, preferably 0.1-4%, more preferably 0.15-2.0% and especially 0.2-1.0%. The cationic part of the ionic surfactant comprises one or more surfactants containing at least 10 carbon atoms in the hydrophobic part of the molecule and at least one amino group or another cationic nitrogen atom (such as in a quaternary ammonium compound). Examples of suitable cationic surfactants are mono-, di- and trivalent amines, ethoxylated amines, quaternary ammonium compounds, ampholytes (amphoteric compounds containing at least one amine group and at least one acid group). A suitable ampholyte is coco alkyl  $\beta$ -amino propionic acid. Examples of especially suitable cationic surfactants are imidazoline derivatives such as 1-(2-hydroxyethyl)-2- $C_{8-22}$ -alkyl- and - $C_{8-22}$ -alkenyl-2-imidazoline, e.g. imidazoline 0 (1-(2-hydroxyethyl)-2-heptadecenyl-2-imidazoline). The molar amount of the amine-containing surfactant in relation to the anionic surfactant should be 5-100%, preferably 10-80% and especially 20-60%. Moreover, the amount of salt should be adjusted so that the pH of the emulsion is in the range of 7.4-10.5, preferably 7.8-10 and especially 8.2-9.5. As a further stabilizer and additive for the resistance to cold, the mould release composition in emulsion form may contain 1-20%, preferably 2-15% and especially 5-10% of one or more glycols and/or glycol ethers and/or polyglycols in which the number of ether groups does not exceed 5. Examples of suitable glycol components are glycerol, propylene glycol, ethylene glycol, butylglycol, propylene glycol methyl ether, cellosolve and diethylene glycol.

The preparation of finished long-term stable release oil emulsions is preferably carried out by dissolving or dispersing the anionic and cationic surfactant in the aqueous phase and adjust the pH of the water to the desired value in the finished emulsion by adding the base corresponding to the finished salt. The non-ionic surfactants are normally dissolved in the oily phase. Optionally, sparingly soluble divalent or trivalent metal salts of  $C_{10-30}$  fatty acids may be incorporated by first dispersing them in the oily phase before the preparation of the emulsion. It is possible to mix and disperse the glycol components in both the oily phase and the aqueous phase before the mixing thereof. The final emulsion is prepared by adding the oily phase into the water phase with stirring. If necessary, the pH may then be adjusted to a higher value by the addition of a base. In order to prepare a long-term stable emulsion, a final intensive processing as stated above is necessary. The preparation is performed at a temperature between -5 and +80° C, preferably a temperature of 5-55°C and especially 10-35°C.

The emulsions described above may be prepared as long-term stable emulsions with a low viscosity. As determined by an Emila viscosimeter, the viscosity at 40°C should be below 40 cP, preferably below 25 cP and especially below 15 cP. At 20°C, the viscosity should be below 60 cP, preferably below 40 cP and especially below 20 cP.

If the final emulsification process is carried out at high temperature, i.e. above 40°C, but depending on the composition, and under vigorous conditions, and if the mixture to be emulsified comprises a surfactant with a relatively low HBL value, an emulsion with a higher viscosity, i.e. above 200 cP, may be obtained. This phenomenon may be due to a formation of an emulsion system consisting of a mixture of both water-in-oil and oil-in-water emulsions, which means that a part of the initially formed oil-in-water emulsion has been converted into a water-in-oil emulsion. It is contemplated that the water-in-oil emulsion is emulsified in the oil-in-water emulsion. It is contemplated that this phenomenon corresponds to the conversion which takes place after the spreading on the mould surface and the evaporation of water as mentioned above.

As mentioned above, it is preferred that the release composition comprises an additive which imparts corrosion protective properties to the composition so as to prevent rust on steel moulds. In a general aspect, the emulsions described above will also be useful as corrosion inhibitors. The corrosion-inhibiting properties may be achieved or improved by increasing the amount of anionic surfactant selected from the group consisting of  $C_{8-22}$  alkyl or  $C_{8-22}$  alkenyl sarcosines,  $C_{6-20}$  alkyl or  $C_{6-20}$  alkenyl succinic acids,  $C_{6-20}$  alkyl or  $C_{6-20}$  alkenylphenoxyacetic acid,  $C_{8-22}$  alkylsul-

famido carboxylic acid, C<sub>1-10</sub> alkylarylsulfamido carboxylic acid and arylsulfamido carboxylic acid, the total amount of anionic surfactant in the composition being 0.5-12% by weight, preferably 1-9.5%, more preferably 2-7%, and especially 3.5% by weight, based on the total composition, and cationic surfactant, the amount of the cationic surfactant being 5-150%, calculated on the basis of the molar amount of the anionic surfactant present in the emulsion. (It will be appreciated that the anionic surfactants may further comprise a carbylene chain in the molecule, which does not appear from their names, i.e. an "aryl sulfamido carboxylic acid" is in fact an "aryl sulfamido carbylene carboxylic acid"). The cationic surfactants of the same type as mentioned above are to be used in an amount of 5-150%, preferably 10-100% and especially 20-50%, on molar basis, calculated on the molar amount of the anionic surfactant.

## 10 TEST METHODS

*Determination of release action and examination of the appearance of the concrete surface and concrete residues in the mould*

15 The retarding effect and the other characteristics as release agents of the compositions to be used in the method according to the invention were determined by an examination of concrete flags moulded in standard moulds under standard conditions.

The mould material was stainless steel, and in the case of oil-in-water emulsions, plywood with a coating meant for moulding of concrete, and the mould size was 350 x 200 x 80 mm. Common plastic concrete with a slump of 90-110 mm, a density of about 2350 kg/m<sup>3</sup> and a content of air of about 2% was used. The amount of applied release agent was about 35 g/m<sup>2</sup>, applied by spraying. The temperature of the release agent was 20°C. The deposition of the concrete was performed 5-15 minutes after the spraying; the concrete was vibrated for about 20 seconds; the curing temperature was 20°C and the curing time 24 hours.

After curing for 24 hours at 20°C, the bodies were demoulded. The release ability was tested in the following way: 25 After removal of the outer frame of the mould, the flag was left on the mould basis. One of the ends of the mould basis was tilted until the flag started to slide down; then the tilting angle was measured. If the flag had not left the basis when it had been tilted to 90°, a tensile test was performed and the force necessary to remove the flag was determined. The bodies were examined for residues of concrete left on the mould and release agent left on the concrete surface, and the ease of cleaning the mould was estimated. The retardation (absence of hardening) of the surface of the concrete body 30 was tested by means of a spring-loaded knife, the paintability was tested by estimating the water-repellance. The amount of discolorations and pores in the surface was determined. The test results were expressed in points in the range of 1-5, and the tilting angle was measured (°). (It appears that a high number of points does not necessarily reflect better properties). The scale used can be explained by the following table:

Scale	1	3	5
Residual concrete in the mould	Much	Normal	Little
Release agent left in the mould	Little	Normal	Much
Mould cleaning properties	Difficult	Normal	Easy
Discolorations on concrete	Many	Normal	Few
Pores in concrete	Many	Normal	Few
Retardation on concrete	Much	Normal	Little
Suitable for painting	Water-repellent	Normal	Water-absorbent

50 The test results based on the scale above are shown in Table 1 which also contains the composition of the release agents used.

The retarding effect of a release agent on concrete can be determined by mixing an amount of release agent in the concrete before moulding it into a test body. When the test body has been cured, a test for bending strength (in MN/m) can be performed. The amount of release agent is stated as % by weight, based on the amount of cement in the mortar mixture 1:3. The reference test is mortar without release agent added, and mortar with a normal commercially available release agent based on mineral oil is used as comparison. The test results are shown in Table II together with results of tests showing the compressive strength (determinations performed in duplicate; mean value stated in the table) and the indices for bending strength and compressive strength, respectively (percentage of the value obtained with concrete

without release agent added). The retarding effect of a release agent is reflected in a decreased strength in this test. The measurements were performed after 1,3 and 7 days at 20°C or after 2, 3, 5, 7, 14 and 28 days.

#### Biodegradability

Biodegradability is expressed as TOD (Theoretical Oxygen Demand) assessed by means of manometric respirometry according to the method described by the Standing Committee of Analysts, Water Research Centre, Streven, GB. The test results are shown in Tables III, IV and V.

#### Viscosity

Viscosity measurements were carried out at 20°C by means of an Emila viscosimeter whereby the viscosity measurements were stated directly in cP. Viscosity measurements of emulsions on a Emila viscosimeter are not very accurate because the viscosimeter itself exerts a certain degree of shear stress which influences the viscosity of the emulsion during the measurement, but the accuracy and reliability of the measurements are sufficient to be relevant in distinguishing between different formulations.

The viscosity of water-in-oil emulsions depends on the intensity of the emulsification process. Differences in measurements on emulsions are partly due to emulsification differences, but addition of viscosity-decreasing agents is so significant that the differences in emulsification are negligible.

#### EXAMPLES

##### Preparation of release agents

#### EXAMPLE 1

A mould release agent of the following composition was prepared:

2-Ethyl-hexyl ester <sup>*)</sup>	94 kg
Refined wool grease	4 kg
Ethoxylated nonylphenol (HLB about 9)	2 kg
<b>Total</b>	<b>100 kg</b>

<sup>\*)</sup> Prepared from an acid mixture consisting of:

Stearic acid:	32%
Palmitic acid:	51%
Myristic acid:	14%
Lauric acid:	3%

and 2-ethyl-hexyl alcohol in stoichiometric amounts.

The ingredients were mixed at ambient temperature by means of a standard mixing apparatus. The resulting mixture was stable for several months.

#### EXAMPLE 2

A mould release agent of the following composition was prepared:

Oily phase:	
2-Ethyl-hexyl ester*)	23 kg
Rape oil	4.6 kg
Mineral oil (Gulfpar 19)	27.6 kg
Non-ionic emulsifier (HLB=3)	4.2 kg
Triethanolamine-oleic acid ester	0.6 kg
Aqueous phase:	
Tap water	39.2 kg
MgSO <sub>4</sub>	0.4 kg
Acrylate solution (40%)	0.4 kg
Total	100.0 kg

\*) The same ester composition as used according to Example 1.

The aqueous phase was dispersed in the oily phase by means of a high-speed mixer of the Silverson type with a peripheral speed of about 1500 meter/minute at 30°C for 10 minutes.

The resulting emulsion was stable.

#### EXAMPLE 3

A mould release agent of the following composition was prepared:

5

3a

3b

3c

Aqueous phase:

Tap water

4900 g

4900 g

4900 g

Stearic acid

70 g

70 g

70 g

10 Imidazoline O<sup>1</sup>

30 g

30 g

30 g

Ammonia ad pH 9

+

+

+

Oil phase:

15 Radia 7131<sup>2</sup>

3950 g

1850 g

3800 g

Risella oil 15<sup>3</sup>

-

2000 g

-

Propylene glycol

500 g

500 g

500 g

20 Berol 26<sup>4</sup>

150 g

150 g

150 g

Berol 259<sup>5</sup>

150 g

150 g

150 g

Grindtek Amos 90<sup>6</sup>

250 g

250 g

250 g

Grindtek MOP 90<sup>7</sup>

100 g

100 g

25 Ceasit I<sup>8</sup>

50 g

Risella

oil

30 Viscosity at 20°C

Emila

25

14.5

15.5

17

Viscosity at 40°C

Emila

12

9.5

11

13

35 Viscosity at 20°C

2.08

1.52

1.41

1.31

Viscosity at 40°C

40

1) Imidazoline O: 1-(2-hydroxyethyl)-2-heptadecenyl-2-imidazoline (Protex)

45 2) Radia 7131: Technical 2-ethylhexyl stearate (Oleofina)

3) Risella oil 15: Paraffinic mineral oil (Shell) (viscosity at 40°C: 15 cSt) (comprises about 1% of aromates)

50 4) Berol 26: Poly (4) ethoxylated nonyl phenol (Berol) (HLB: 8.9)

5) Berol 259: Poly (2) ethoxylated nonyl phenol (Berol) HLB: 5.7)

- 6) Grindtek Am s 90: Acetylated monoglyceride prepared from lard  
(Grindsted Products)
- 7) Grindtek MOP 90: Fatty acid monoglyceride prepared from lard  
(Grindsted Products)
- 8) Ceasit I: Micronized Ca-stearate (Chemische Werke München).

The oily phase was mixed into the aqueous phase with stirring. The mixture was homogenized in a high-pressure emulsifier at 200 bar. The inlet temperature was 26°C, and the outlet temperature was 35°C. The high-pressure emulsifier was APV Gaulin, Type Lab 60/500/2 with a capacity of 60 l/h and a pressure  $P_{\max}$  of 500 bar.

Risella oil (Shell) is a low-viscous paraffinic mineral oil with a viscosity of 15 cSt at 40°C (according to specifications from Shell). Risella has been used as a reference in the above measurements. The comparison shows especially that the aqueous emulsions are much less temperature-dependent than is the mineral oil. This is advantageous when the emulsions are to be used at low temperatures.

All release agents used in the tests described below were prepared as described in Example 1, Example 2, or Example 3.

#### TEST RESULTS

##### *Releasing characteristics*

Mould release compositions in non-emulsified form and with the composition stated in Table I below were applied to the standard steel moulds and mould release compositions in emulsion form of compositions as stated in Tables IIa, IIb and IIc, respectively, were applied to standard steel and plywood moulds by means of a normal spraying device for liquids, in an amount of 35 g/m<sup>2</sup>. Thereafter, common plastic concrete was poured into the moulds and left to cure and thereafter tested as described above under TEST METHODS. The results appear from Tables I, IIa, IIb, and IIc, wherein S = stainless steel, and P = plywood.

Table I

Test No.	1	2	3	4	5	6	7	8
Untreated	*							
Soy oil		100						
Linseed oil			100					
Isobutyl stearate				100				
Mineral oil					80			
Aliphatic kerosene					20			
2-ethyl-hexyl oleate						100		
2-ethyl-hexyl palmitate							92	46
Low viscous liquid								
refined paraffin oil								46
Wool grease							8	8
Ethoxylated nonyl-phenol (HLB about 9)								
Tall oil acid								
Oleic acid								
Tilting angle, °	>90	60	40	40	>90	65	20	20
Residual concrete								
in the mould	1	2	3	3	3	3	4	4
Release agent left								
in the mould	-	3	3	3	2	3	2	2
Mould cleaning								
properties	1	2	3	3	3	2	5	4
Discolorations on								
concrete	4	2	3	1	2	3	3	3
Pores in concrete	3	4	3	1	2	3	3	3
Retardation of concrete	5	1	1	5	3	3	3	3
Suitable for painting	5	2	2	2	3	3	2	3

"Mineral oil" is a spindle oil sold under the name Gulfpar 19.

Test No.	9	10	11	12	13	14	15	16
5								
10								
15								
20								
25								
30								
35								
40								
45								
50								
55								



Table IIa

Test No.	113	115	117	118	120
Composition:					
Water	47.6	47.6	47.6	47.6	47.6
Glycerol	4	4	4	4	4
Propylene glycol	4	4	4	4	4
Radia 7131 <sup>1</sup>	40	40	40	40	40
Stearic acid	0.4				0.4
Dimerised oleic/linoleic acid		0.4			
Gafac RE 410 <sup>2</sup>			0.4		
Dodecylbenzene sulphonic acid				0.4	
Berol 26 <sup>3</sup>	4	4	4	4	4
NH <sub>3</sub> ad pH 8.5	+	+	+	+	
Monoethanol amine ad pH 9					+
Mould Material	S P	S P	S P	S P	S P
Tilting angle, °	35 29	34 33	32 25	80 32	24 28
Residual concrete in the mould	5 5	3 1	3 2-3	1 1	5 5
Release agent left in the mould	1 1	1 2	1 1	1 1	1 1
Mould cleaning proper ties	5 5	4 4	3-4 5	4-5 4-5	5 5
Discolorations on concrete	5 5	4* 3*	5* 5*	12* 1-2*	5 5
Pores in concrete	4-5 4-5	5 4	5 5	3 3	5 5
Retardation of concrete	5 5	3 3	3 3	3 3	5 5
Suitable for painting	5 5	5 5	5 5	5 5	5 5

\* - Blotches in the edge owing to the fact that the release composition did not adhere sufficiently to the mould

Table IIb

Test No.	119		127		128		129		134	
Composition:										
Water	47.6		47.6		57.5		47.5		47.6	
Glycerol	4		4		4		4		4	
Propylene glycol	4		4		4		4		4	
Radia 7131 <sup>1</sup>	40				30		40		20	
Risella oil 15			40						20	
Berol 724	0.4									
Stearic acid			0.4		0.5					0.4
Crodacinic L <sup>6</sup>							0.5			
Berol 26 <sup>3</sup>	4		4		4		4		4	
NaOH ad pH 9	+									
NH <sub>3</sub> ad pH 8.5			+		+		+		+	
Mould Material										
	S	P	S	P	S	P	S	P	S	P
Tilting angle, °	32	30	90	38	90	34	26	32	28	36
Residual concrete in the mould										
	3	3	4	4	4	4	4	2	3	4-5
Release agent left in the mould										
	1	1	4	3	3	2	1	2	3-4	1
Mould cleaning proper ties										
	4	4	1-2	3-4	3	4-5	3	4	2-3	4-5
Discoloration on concrete										
	3	3	5	5	5	4-5	2	2	4-5	5
Pores in concrete										
	4-5	5	4	4	5	4	3	2	4-5	4-5
Retardation of concrete										
	3	3	3-4	3-4	4	4	3	3	3	3
Suitable for painting										
			4	4	4	4	3	3	4	4

Table IIc

Test No.	166	168	169	173	175
Composition:					
Water	47.6	47.5	50.5	49.5	48.5
Glycerol	4	4			
Propylene glycol	4	4	5	5	5
Radia 7131 <sup>1</sup>	40	40	39.7	39.7	39.7
Berol 26 <sup>3</sup>	4	2	1	1.5	1.5
Berol 259 <sup>7</sup>			1	1.5	1.5
Grindtek					
Amos 90 <sup>8</sup>		2	2	2	3
Stearic acid	0.4	0.5	0.5	0.5	0.5
Imidazoline 0 <sup>9</sup>		0.3	0.3	0.3	0.3
NH <sub>3</sub> ad pH	8.7	9.1	9.3	9.3	9.2
Viscosity (Emila)	12 cP	10 cP	10 cP	10 cP	10 cP
Mould Material	S P	S P	S P	S P	S P
Tilting angle, °	90 74	28 55	33 31	35 40	30 35
Residual concrete in the mould	3 1	3 2-3	3-4 4-5	3-4 3-4	3-4 3-4
Release agent left in the mould	2 2	2 2-3	2 1	2 1	2 1
Mould cleaning properties	2 1	5 5	5 5	5 5	5 5
Discoloration on concrete	5 1	5 5	5 5	5 5	5 5
Pores in concrete	5 4	5 5	5 5	5 5	5 5
Retardation of concrete	4 4	2 2	2 2	2 2	2 2
Suitable for painting	5 5	5 5	5 5	5 5	5 5

- 1) Radia 7131: Technical 2-ethylhexyl stearate (Oleofina)
- 2) Gafac RE 410: Mono/diphosphoric acid ester (GAF)
- 5 3) Berol 26: Poly (4) ethoxylated nonylphenol (Berol) (HLB: 8.9)
- 4) Risella Oil: Paraffinic mineral oil (Shell) (viscosity at 40°C: 15 cSt)
- 10 5) Berol 724: Mixed phosphoric acid ester (Berol)
- 6) Crodacinic L: N-lauryl sarcosine (Croda)
- 7) Berol 259: Ethoxylated nonyl phenol (Berol) (HLB: 5.7)
- 15 8) Grindtek Amos 90: Acetylated monoglyceride prepared from lard (Grindsted Products)
- 9) Imidaxoline O: 1-(2-Hydroxyethyl)-2-heptadecenyl-2-imidazoline (Protex)

The tests referred to in Tables IIa and IIb indicate that especially compositions containing 0.4-0.5% of stearic acid in the form of a salt have the most advantageous release properties.

25 From the results stated in Table IIa, obtained after a curing period of 17 hours, it appears that the addition of Grindtek Amos 90 and Imidaxoline O has an advantageous effect on the release ability, and that a reduction in the contents of Berol 26 and glycerol (anti-freeze) apparently has an advantageous effect. A certain retardation of the concrete surface could be observed, but the surface appearance was good, and the residues in the mould were easily removable.

#### 30 Retarding effect

The retarding effect on concrete was determined as described above in TEST METHODS using the amounts stated below.

35 Table III shows the results obtained, i.e. the density of the concrete bodies formed, the bending strength and the compression strength, and furthermore indexes of bending strength and compressive strength, i.e. the result obtained stated as a percentage of the result obtained in a concrete body formed without a release agent.

The compositions were as follows:

#### 40 Test No.

- 1: No agent added (reference test)
- 2: 2.5% of a mineral oil product
- 3: 5% of a mineral oil product
- 45 4: 10% of a mineral oil product
- 5: 5% of soy oil
- 6: 10% of soy oil
- 7: 5% of linseed oil
- 8: 10% of linseed oil
- 50 9: 5% of isobutyl stearate
- 10: 10% of isobutyl stearate
- 11: No agent added (reference test)
- 12: 10% consisting of 50% of mineral oil (Gulpar 19) and 50% of 2-ethyl-hexyl stearate
- 13: 20% consisting of 50% of mineral oil (Gulpar 19) and 50% of 2-ethyl-hexyl stearate
- 55 14: 10% of a mineral oil mixture (consisting of 80% of spindle oil and 20% of kerosene)
- 15: 10% of a mineral oil mixture (consisting of 72 parts of spindle oil, 20 parts of kerosene and 8 parts of tall oil [retarding agent])
- 16: 10% of a mineral oil mixture (consisting of 80% paraffin oil and 20% of kerosene)

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- 17: 10% of a mineral oil mixture (consisting of 72 parts of paraffin oil, 20 parts of kerosene and 8 parts of tall oil [retarding agent])
- 18: 10% ethyl-hexyl stearate
- 19: 10% consisting of 50% ethyl-hexyl stearate and 50% of paraffin mineral oil
- 5 20: 10% of 2-ethyl-hexyl oleate
- 21: 10% consisting of 50% ethyl-hexyl oleate and 50% mineral oil (Gulpar 19)
- 22: = 18
- 23: = 21
- 24: 10% of isobutyl oleate
- 10 25 : 10% of propylene glycol dioleate
- 26: 5% of methyl oleate

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Table III

T st No.	Days	Density kg/m <sup>2</sup>	B nding strength MN/m <sup>2</sup>	Compres- sive strength MN/m <sup>2</sup>	Bending index %	Compres- sive index %
1	1	2203	4.75	21.50	100	100
2	1	2137	4.40	17.72	93	82
3	1	2132	4.20	15.60	88	73
4	1	2133	3.40	12.16	72	57
5	1	2137	3.10	11.07	65	51
6	1	2145	2.70	8.60	57	40
7	1	2148	2.30	8.11	48	38
8	1	2141	1.50	4.86	32	23
9	1	2129	3.80	14.07	80	65
10	1	2031	2.95	11.91	62	55
1	3	2250	6.60	39.07	100	100
2	3	2164	5.95	31.25	90	80
3	3	2164	6.00	27.51	91	70
4	3	2148	5.40	23.47	82	60
5	3	2153	4.50	18.57	68	48
6	3	2164	3.60	13.16	55	34
7	3	2168	3.40	13.72	52	35
8	3	2180	1.90	6.66	29	17
9	3	2152	5.85	22.51	89	58
10	3	2043	4.20	20.07	64	51

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Table III continued

5	1	7	2230	7.30	40.82	100	100
	2	7	2172	6.70	32.32	92	80
	3	7	2203	6.60	31.26	90	79
	4	7	2164	5.85	26.63	80	65
10	5	7	2145	5.40	24.01	74	60
	6	7	2164	3.85	15.44	53	39
	7	7	2180	4.35	18.75	60	46
15	8	7	2195	2.35	8.63	32	22
	9	7	2148	5.90	29.44	81	65
	10	7	2074	4.80	24.82	66	63
20	11	2	2273	5.95	27.3	100	100
		3	2234	6.65	32.9	100	100
		5	2214	7.10	40.4	100	100
		7	2214	7.50	41.5	100	100
25		14	2242	7.30	40.8	100	100
		28	2246	7.75	44.2	100	100
30	12	2	2188	5.80	20.2	97	74
		3	2184	5.70	25.1	86	76
		5	2125	5.40	27.6	76	68
		7	2211	6.20	31.0	83	75
35		14	2164	6.50	31.9	89	78
		28	2188	6.80	32.8	88	74
40	13	2	2125	3.80	15.9	56	58
		3	2137	5.00	20.9	75	64
		5	2160	5.70	25.2	80	62
		7	2129	5.30	26.2	71	63
45		14	2102	5.80	24.8	79	61
		28	2137	6.30	27.0	81	61

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Table III continued

5	14	1	2137	4.10	14.0	86	65
		3	2148	6.20	30.0	93	91
		7	2152	6.60	31.5	88	76
10	15	1	2133	0.40	1.5	8	7
		3	2141	0.9	3.1	14	9
		7	2125	1.30	5.7	17	14
15	16	1	2184	4.00	14.0	84	65
		3	2184	6.30	29.8	95	91
		7	2168	7.00	31.7	93	76
20	17	1	2121	0.90	3.3	19	15
		3	2172	2.55	10.2	38	31
		7	2148	3.20	14.3	43	34
25	18	1	2172	3.15	11.5	66	53
		3	2164	5.65	27.2	85	83
		7	2187	5.55	29.4	74	71
30	19	1	2148	3.10	11.6	65	54
		3	2176	5.70	26.2	86	80
35		7	2156	6.50	30.3	87	73
	20	1	2148	3.00	11.1	63	52
		3	2195	6.10	23.8	92	72
40		7	2168	6.60	27.8	88	67
45	21	1	2156	3.20	10.3	67	48
		3	2168	5.50	25.9	83	79
		7	2156	6.35	29.0	85	70

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Table III c ntinued

5	22	1	2152	2,90	10.3	61	48
		3	2184	5.40	24.3	81	74
		7	2199	6.45	30.9	86	74
10	23	1	2168	3.05	9.9	64	46
		3	2180	5.55	24.3	83	74
		7	2184	6.10	29.4	81	71
15	24	1	2160	3.9	15.2	82	71
		3	2140	5.6	27.4	85	83
20		7	2168	5.9	29.1	79	70
	25	1	2140	1.5	4.7	32	22
25		3	2160	2.2	8.7	33	26
		7	2176	3.5	15.2	47	37
30	26	1	2125	0.7	2.8	15	13
		3	2172	1.9	7.0	29	21
		7	2145	2.3	8.3	31	20

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The test referred to above show that mineral oil *per se* has only a very slight retarding effect on concrete. The addition of tall oil to mineral oil products imparts a strong retarding effect to the concrete. Isobutyl stearate, 2-ethylhexyl stearate and 2-ethylhexyl stearate have only a limited retarding effect. Vegetable oils (soy oil and especially linseed oil), propylene glycol dioleate and methyl oleate have a very strong retarding effect which in some cases will be too strong.

#### Biodegradability

Biodegradability determinations were performed on different concrete release agents with compositions as stated in tables IV, V and VI below. The determination of TOD values were carried out every second day for 28 consecutive days. Each determination was carried out in duplicate together with a reference test (in duplicate) and a blind test (in duplicate). In tables IV, V and VI mean values of the TOD determinations are stated.

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Biodegradability, % TOD

Table IV

Test No.	3x	6x	4x	5x
Emulsifier*	4%	4%	4%	4%
Spindle oil	0%	24%	48%	72%
Isobutyl stearate	96%	72%	48%	24%
Days	% TOD	% TOD	% TOD	% TOD
2	10.5	9	10.5	7
4	27	20.5	20.5	11.5
6	39	29.5	26	12
8	50	39.5	31.5	16
10	60	46	36	21.5
12	63	46	36.5	22.5
14	67	48.5	40	25
16	71.5	51.5	45.5	29.5
18	74	54	47	32
20	75.5	55	47	33.5
22	76	56	49	34
24	80	58	51.5	37
26	80	59.5	51.5	36
28	81.5	61	52	37

\* Low-ethoxylated nonylphenol

Table V

Test No.	4x	7x	8x	9x
Emulsifier*	4%	4%	4%	4%
Spindle oil	48%			48%
White oil**			48%	
Odourless white spirit		48%		
Isobutyl stearate	48%	48%	48%	
Soy oil				48%
Days	% TOD	% TOD	% TOD	% TOD
2	7	7	7	6
4	16	16	17	14
6	23	22	23	19
8	28	28	29	23
10	31	33.5	34	25.5
12	33	38	38	28
14	34.5	43	40.5	28
16	35.5	46.5	43	29.5
18	36.5	50	46	30.5
20	37	52	48	31.5
22	38	52.5	49.5	33
24	39	54.5	50	34
26	41	56.5	51.5	35.5
28	42	57	51.5	36

\* Low-ethoxylated nonylphenol

\*\* White oil free from aromatic compounds

Table VI

Test No.	10x	12x	11x	13x
Emulsifier*	4%	4%	4%	4%
White oil**		24%	48%	72%
2-Ethylhexyl stearate	96%	72%	48%	24%
Days	% TOD	% TOD	% TOD	% TOD
2	8	6.5	10	6
4	20.5	18	20	11.5
6	28.5	23.5	23.5	12.5
8	33	25	25	12.5
10	40	30.5	29.5	17
12	44	35.5	34.5	19
14	45.5	35.5	33.5	18
16	51	39	35.5	20
18	56.5	42	38	23.5
20	57	41	36.5	22.5
22	59	42	37.5	24
24	62.5	43	39	28
26	64	42.5	38.5	28.5
28	64.5	44	39	29

\* Low-ethoxylated nonylphenol

\*\* White oil free from aromatic compounds

Compositions with a high content of synthetic esters of aliphatic carboxylic acids are more biodegradable than compositions with a high content of mineral oils, and as appears from table III, the compositions with synthetic esters have advantageous properties with respect to retarding effect.

#### Viscosity

Viscosity measurements were performed as described under TEST METHODS above on mixtures of natural vegetable oils with synthetic esters and on water-in-oil emulsions in which the oily phases were natural vegetable oils, optionally in admixture with mineral oils. The compositions and results appear from the tables below.

	Rape oil, %	100	95	90	80	70	60	40	20	0
5	2-Ethyl-hexyl ester*, %	0	5	10	20	30	40	60	80	100
	Viscosity, cP	65	62	51	42	35	30	22	15	11
10	Soy oil, %	100	95	90	80	70	60	40	20	0
	2-Ethyl-hexyl ester, %	0	5	10	20	30	40	60	80	100
15	Viscosity, cP	45	41	38	34	29	25	19	14	11

\* The ester was prepared from an acid mixture consisting of:

20	Stearic acid:	32%
	Palmitic acid:	51%
	Myristic acid:	14%
25	Lauric acid:	3%

30 Water-in-oil emulsions

1.

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	Oily phase:					
40	2-Ethyl-hexyl palmitate	18.4%	23%	27.6%	32.2%	36.8%
	Rape oil					
	Purified mineral oil (Gulpar 19)	18.4%	23%	27.6%	32.2%	36.8%
	Non-ionic emulsifier (HLB=3)	2.8%	3.5%	4.2%	4.9%	5.6%
45	Triethanolamine-oleic acid ester	0.4%	0.5%	0.6%	0.7%	0.8%
	Aqueous phase:					
	Tap water	58.8%	49%	39.2%	29.4%	19.6%
	MgSO <sub>4</sub>	0.6%	0.5%	0.4%	0.3%	0.2%
50	40% acrylate solution	0.6%	0.5%	0.4%	0.3%	0.2%
	Viscosity, cP	475	210	130	80	55

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2.

5	Oily phase:					
	2-Ethyl-hexyl palmitate					
	Rape oil	18.4%	23%	27.6%	32.2%	36.8%
10	Purified mineral oil (Gulfpar 19)	18.4%	23%	27.6%	32.2%	36.8%
	Non-ionic emulsifier (HLB=3)	2.8%	3.5%	4.2%	4.9%	5.6%
	Triethanolamine oleic acid ester	0.4%	0.5%	0.6%	0.7%	0.8%
	Aqueous phase:					
15	Tap water	58.8%	49%	39.2%	29.4%	19.6%
	MgSO <sub>4</sub>	0.6%	0.5%	0.4%	0.3%	0.2%
	40% acrylate solution	0.6%	0.5%	0.4%	0.3%	0.2%
20	Viscosity, cP	>1000	360	260	185	150

3.

25	Oily phase:					
	2-Ethyl-hexyl palmitate	23%	18.4%	13.8%	9.2%	4.6%
	Rape oil	4.6%	9.2%	13.8%	18.4%	23%
30	Purified mineral oil (Gulfpar 19)	27.6%	27.6%	27.6%	27.6%	27.6%
	Non-ionic emulsifier (HLB=3)	4.2%	4.2%	4.2%	4.2%	4.2%
	Triethanolamine oleic acid ester	0.6%	0.6%	0.6%	0.6%	0.6%
35	Aqueous phase:					
	Tap water	39.2%	39.2%	39.2%	39.2%	39.2%
	MgSO <sub>4</sub>	0.4%	0.4%	0.4%	0.4%	0.4%
40	40% acrylate solution	0.4%	0.4%	0.4%	0.4%	0.4%
	Viscosity, cP	155	175	215	225	370

It appears from the tables that as little as 10% of synthetic ester added to a natural vegetable oil gives a considerable decrease in viscosity, and that as little as 5% (calculated on the total content) in the emulsified systems gives an advantageous decrease in viscosity.

### Claims

1. A method for improving the release of a moulded concrete body from the mould by applying an effective amount of a concrete release composition to the mould, said composition being an oil-in-water emulsion containing water in an amount of 10-90% by weight of the total emulsion, an oily component in an amount of 10-90% by weight of the total emulsion, one or more non-ionic surfactants in an amount of 0.5-20% by weight of the total emulsion, and one or more anionic surfactants provided as a sodium, potassium, lithium, ammonium or a lower alkylamine, lower alkyl-alkanolamine or lower alkanolamine salt of at the most 8 carbon atoms or a mixed salt, in which the amount of the anionic surfactant in relation to the non-ionic surfactant is 1:100% by weight. and with the proviso that the sum of ingredients in the composition does not exceed 100%.
2. A method according to claim 1 in which the oily component is a mineral oil.

3. A method according to claim 2 in which the mineral oil comprises at the most 9% of aromatics.
4. A method according to claim 2 in which the mineral oil has a boiling point of at least 250°C.
- 5 5. A method according to claim 1 in which the oily component is a triglyceride with 10-24 carbon atoms in each fatty acid moiety, optionally in admixture with a mineral oil.
6. A method according to claim 5 in which the ratio between mineral oil and triglyceride with 10-24 carbon atoms in each fatty acid moiety is from 99:1 to 50:50.
- 10 7. A method according to claim 1 in which the oily component comprises an ester of an aliphatic carboxylic acid with a mono- or dihydric alcohol, the total number of carbon atoms in the esters being 8-46, and having a melting point of at the most 35°C.
- 15 8. A method according to claim 1 in which the ester constitutes 1-100% of the oily component, the remaining part being mineral oil and/or a triglyceride with 10-24 carbon atoms in each fatty acid moiety.
9. A method according to any of claims 1-8 in which the content of oily component is 15-75%, preferably 25-55%, by weight of the total emulsion.
- 20 10. A method according to any of claims 1-9 in which the amount of the anionic surfactant calculated in relation to the amount of the non-ionic surfactant on weight basis is 2-50%, especially 4-25%.
11. A method according to any of claims 1-9 in which the amount of anionic surfactant is 0.05-6% by weight, preferably 0.1-4%, more preferably 0.15-2%, and especially 0.2-1%, by weight of the total emulsion.
- 25 12. A method according to any of claims 1-11 in which the anionic surfactant is a salt of a mono- or diphosphoric acid ester of an ethoxylated C<sub>4-15</sub> alkylphenol, ethoxylated di-C<sub>2-15</sub> alkylphenol or an ethoxylated fatty C<sub>8-22</sub> alcohol.
- 30 13. A method according to any of claims 1-11 in which the anionic surfactant is selected from the group consisting of salts of C<sub>8-22</sub> alkylsarcosines, C<sub>1-15</sub> alkylphenylcarboxylic acids, arylcarboxylic acids, aryl-C<sub>1-15</sub> alkylcarboxylic acids, C<sub>1-15</sub> alkylaryl-C<sub>1-15</sub> alkylcarboxylic acids, phenoxy-C<sub>1-15</sub> alkylcarboxylic acids, C<sub>1-15</sub> alkylphenoxy-C<sub>1-15</sub> alkylcarboxylic acids, C<sub>8-30</sub> alkylcarboxylic acids and the corresponding dicarboxylic acids and the corresponding unsaturated analogues thereof and salts of unsaturated dimerised or trimerised acids.
- 35 14. A method according to claim 10 or 11 in which the anionic surfactant is a salt of a saturated C<sub>12-30</sub> acid such as lauric, myristic, palmitic and stearic acid.
15. A method according to any of claims 1-14 in which the amount of non-ionic surfactant(s) is 1-12% by weight of the total emulsion, preferably 2-7% by weight.
- 40 16. A method according to claim 15 in which the non-ionic surfactant(s) is/are selected from ethoxylated, propoxylated or co-ethoxylated/propoxylated surfactants with a Hydrophil-Lipophil Balance corresponding to an HLB value of from 5.0 to 11.
- 45 17. A method according to claim 16 in which the HLB value is from 5.5 to 9.9, preferably from 6.0 to 9.0.
18. A method according to claims 1-15 in which the non-ionic surfactant composition comprises at least one member of the group consisting of surfactants as defined in claim 16 or 17, monoglycerides of saturated and unsaturated C<sub>8-24</sub> fatty acids, optionally bearing a hydroxy group, and mono- or di-(C<sub>1-4</sub>)-acylated monoglycerides of C<sub>2-24</sub> fatty acids, optionally bearing a hydroxy group.
- 50 19. A method according to any of claims 1-15 in which the non-ionic surfactant composition comprises a mono- or di-(C<sub>1-4</sub>)-acylated monoglyceride of C<sub>2-24</sub> fatty acids, optionally bearing a hydroxy group, and optionally one or more surfactants as defined in claim 16 and/or one or more monoglycerides of saturated or unsaturated C<sub>8-24</sub> fatty acids, optionally bearing a hydroxy group.
- 55 20. A method according to any of claims 16-19 in which the ethoxylated surfactant(s) is are selected from the group

consisting of ethoxylated nonylphenol, ethoxylated dinonylphenol, ethoxylated C<sub>8-22</sub> fatty alcohols and C<sub>10-22</sub> fatty acid polyethylene glycol esters.

21. A method according to any of claims 1-20 in which the emulsion further comprises a cationic surfactant with at least 10 carbon atoms in the hydrophobic part of the molecule, in an amount of 5-100% based on the molar amount of the anionic surfactant.

22. A method according to claim 21 in which the cationic surfactant is selected from the group consisting of mono-, di- and trivalent alkylamines, ethoxylated amines, quaternary ammonium compounds, and ampholytes,

23. A method according to claim 22 in which the cationic surfactant is an imidazoline derivative such as 1-(2-hydroxyethyl)-2-C<sub>8-22</sub> alkyl or -C<sub>8-22</sub> alkenyl-2-imidazoline.

24. A method according to any of claims 1-23 in which the emulsion further comprises stabilizers, anti-freezes, corrosion-inhibitors, and hydrophobicity-imparting agents.

25. A method according to claim 24 in which the emulsion further comprises one or more glycols and/or glycol ethers and/or polyglycols in which the number of ether groups does not exceed 5, and/or glycerol in an amount of 1-20% by weight of the total emulsion,

26. A method according to any of claims 1-24 in which the emulsion has a viscosity of at the most 40 cP when measured at 40° C on an Emila viscosimeter.

27. A method according to any of claims 1-26 in which the emulsion further comprises an anionic surfactant selected from the group consisting of C<sub>8-22</sub> alkyl or C<sub>8-22</sub> alkenyl sarcosines, C<sub>6-20</sub> alkyl or C<sub>6-20</sub> alkenyl succinic acids, C<sub>6-20</sub> alkyl or C<sub>6-20</sub> alkenylphenoxyacetic acid, C<sub>8-22</sub> alkylsulfamido carboxylic acid, C<sub>1-10</sub> alkylarylsulfamido carboxylic acid and arylsulfamido carboxylic acid, the total amount of anionic surfactant being 0.5-12% by weight, and the amount of the cationic surfactant being 5-150% calculated on the basis of the molar amount of the anionic surfactant present in the emulsion.

28. A method according to any of claims 1-27 in which the pH of the emulsion is 7.4-10.5, preferably 7.8-10, and more preferably 8.2-9.5.

29. A method according to any of claims 1-28 in which the emulsion is applied to the mould in the amount of 10-100 g/m<sup>2</sup>, especially 20-50 g/m<sup>2</sup>.

30. A method for improving the release of a moulded concrete body from the mould by applying an effective amount of an oil-in-water emulsion prepared by addition of water to an emulsion concentrate as defined in any of claims 1-28, without the content of water.

#### Patentansprüche

1. Verfahren zum Verbessern der Freigabe eines geformten Betonkörpers aus der Form durch Aufbringen einer wirksamen Menge einer Betonfreigabezusammensetzung auf die Form, wobei die Zusammensetzung eine Öl-in-Wasser-Emulsion ist, die Wasser in einer Menge von 10 bis 90 Gew% der gesamten Emulsion, eine ölige Komponente in einer Menge von 10 bis 90 Gew% der gesamten Emulsion, ein oder mehrere nichtionische oberflächenaktive Mittel in einer Menge von 0,5 bis 20 Gew% der gesamten Emulsion und ein oder mehrere anionische oberflächenaktive Mittel in Form eines Natrium-, Kalium-, Lithium-, Ammonium- oder Niederalkylamin-, Niederalkylalkanolamin- oder Niederalkanolaminsalz mit höchstens 8 Kohlenstoffatomen oder in Form eines gemischten Salzes enthält, worin die Menge des anionischen oberflächenaktiven Mittels bezüglich des nichtionischen oberflächenaktiven Mittels 1 bis 100 Gew% beträgt, mit der Maßgabe, daß die Summe der Bestandteile in der Zusammensetzung 100 % nicht überschreitet.

2. Verfahren nach Anspruch 1, in dem die ölige Komponente ein Mineralöl ist.

3. Verfahren nach Anspruch 2, in dem das Mineralöl höchstens 9 % Aromaten enthält.

4. Verfahren nach Anspruch 2, in dem das Mineralöl einen Siedepunkt von mindestens 250 °C aufweist.



5. Verfahren nach Anspruch 1, in dem die ölige Komponente ein Triglycerid mit 10 bis 24 Kohlenstoffatomen in jedem Fettsäurerest, gegebenenfalls im Gemisch mit einem Mineralöl, ist.
- 5 6. Verfahren nach Anspruch 5, in dem das Verhältnis zwischen Mineralöl und Triglycerid mit 10 bis 24 Kohlenstoffatomen in jedem Fettsäurerest 99 : 1 bis 50 : 50 beträgt.
7. Verfahren nach Anspruch 1, in dem die ölige Komponente einen Ester einer aliphatischen Carbonsäure mit einem ein- oder zweiwertigen Alkohol, wobei die Gesamtanzahl der Kohlenstoffatome in den Estern 8 bis 46 beträgt, enthält und einen Schmelzpunkt von höchstens 35 °C aufweist.
- 10 8. Verfahren nach Anspruch 1, in dem der Ester 1 bis 100 % der öligen Komponente ausmacht, wobei der restliche Teil Mineralöl und/oder ein Triglycerid mit 10 bis 24 Kohlenstoffatomen in jedem Fettsäurerest ist.
9. Verfahren nach einem der Ansprüche 1 bis 8, in dem der Gehalt an ölige Komponente 15 bis 75 Gew%, vorzugsweise 25 bis 55 Gew%, der gesamten Emulsion beträgt.
- 15 10. Verfahren nach einem der Ansprüche 1 bis 9, in dem die Menge des anionischen oberflächenaktiven Mittels, berechnet in bezug auf die Menge des nichtionischen oberflächenaktiven Mittels auf Gewichtsbasis, 2 bis 50 Gew%, insbesondere 4 bis 25 Gew%, beträgt.
- 20 11. Verfahren nach einem der Ansprüche 1 bis 9, in dem die Menge des anionischen oberflächenaktiven Mittels 0,05 bis 6 Gew%, vorzugsweise 0,1 bis 4 Gew%, insbesondere 0,15 bis 2 Gew% und ganz besonders bevorzugt 0,2 bis 1 Gew%, der gesamten Emulsion, beträgt.
- 25 12. Verfahren nach einem der Ansprüche 1 bis 11, in dem das anionische oberflächenaktive Mittel ein Salz eines Mono- oder Diphosphorsäureesters eines ethoxylierten C<sub>4-15</sub>-Alkylphenols, ethoxylierten Di-C<sub>2-15</sub>-Alkylphenols oder eines ethoxylierten C<sub>8-22</sub>-Fettalkohols ist.
- 30 13. Verfahren nach einem der Ansprüche 1 bis 11, in dem das anionische oberflächenaktive Mittel aus der Gruppe ausgewählt ist, bestehend aus Salzen von C<sub>8-22</sub>-Alkylsarkosinen, C<sub>1-15</sub>-Alkylphenylcarbonsäuren, Arylcarbonsäuren, Aryl-C<sub>1-15</sub>-alkylcarbonsäuren, C<sub>1-15</sub>-Alkylaryl-C<sub>1-15</sub>-alkylcarbonsäuren, Phenoxy-C<sub>1-15</sub>-alkylcarbonsäuren, C<sub>1-15</sub>-Alkylphenoxy-C<sub>1-15</sub>-alkylcarbonsäuren, C<sub>8-30</sub>-Alkylcarbonsäuren und den entsprechenden Dicarbonsäuren sowie den entsprechenden ungesättigten Analogen hiervon und Salzen ungesättigter dimerisierter oder trimerisierter Säuren.
- 35 14. Verfahren nach Anspruch 10 oder 11, bei dem das anionische oberflächenaktive Mittel ein Salz einer gesättigten C<sub>12-30</sub>-Säure, wie Laurin-, Myristin-, Palmitin- und Stearinsäure ist.
- 40 15. Verfahren nach einem der Ansprüche 1 bis 14, in dem die Menge des nichtionischen oberflächenaktiven Mittels oder der nichtionischen oberflächen Mittel 1 bis 12 Gew% der gesamten Emulsion, vorzugsweise 2 bis 7 Gew%, beträgt.
- 45 16. Verfahren nach Anspruch 15, in dem das nichtionische oberflächenaktive Mittel oder die nichtionischen oberflächenaktiven Mittel aus ethoxylierten, propoxylierten oder co-ethoxylierten-propoxylierten oberflächenaktiven Mitteln mit einem Hydrophilic-Lipophilic-Balance-System entsprechend einem HLB-Wert von 5,0 bis 11 ausgewählt wird bzw. werden.
17. Verfahren nach Anspruch 16, in dem der HLB-Wert 5,5 bis 9,9, vorzugsweise 6,0 bis 9,0, beträgt.
- 50 18. Verfahren nach den Ansprüchen 1 bis 15, in dem die Zusammensetzung des nichtionischen oberflächenaktiven Mittels mindestens ein Glied der Gruppe enthält, bestehend aus oberflächenaktiven Mitteln gemäß der Definition im Anspruch 16 oder 17, Monoglyceriden von gesättigten und ungesättigten C<sub>8-24</sub>-Fettsäuren, gegebenenfalls eine Hydroxylgruppe tragend, sowie mono- oder di-(C<sub>1-4</sub>)-acylierten Monoglyceriden von C<sub>2-24</sub>-Fettsäuren, gegebenenfalls eine Hydroxylgruppe tragend.
- 55 19. Verfahren nach einem der Ansprüche 1 bis 15, in dem die Zusammensetzung des nichtionischen oberflächenaktiven Mittels ein mono- oder di-(C<sub>1-4</sub>)-acyliertes Monoglycerid von C<sub>2-24</sub>-Fettsäuren, gegebenenfalls eine Hydroxylgruppe tragend, sowie gegebenenfalls ein oder mehrere oberflächenaktiv Mittel gemäß der Definition im

Anspruch 16 und/oder ein oder mehrere Monoglyceride von gesättigten oder ungesättigten C<sub>8-24</sub>-Fettsäuren, gegebenenfalls eine Hydroxylgruppe tragend, enthält.

20. Verfahren nach einem der Ansprüche 16 bis 19, in dem das ethoxylierte oberflächenaktiv Mittel oder die ethoxylierten oberflächenaktiven Mittel aus der Gruppe ausgewählt ist bzw. sind, bestehend aus ethoxyliertem Nonylphenol, ethoxyliertem Dinonylphenol, ethoxylierten C<sub>8-22</sub>-Fettalkoholen und C<sub>10-22</sub>-Fettsäurepolyethylenglykolestern.

21. Verfahren nach einem der Ansprüche 1 bis 20, in dem die Emulsion ferner ein kationisches oberflächenaktives Mittel mit mindestens 10 Kohlenstoffatomen im hydrophoben Teil des Moleküls in einer Menge von 5 bis 100 %, bezogen auf die molare Menge des anionischen oberflächenaktiven Mittels, enthält.

22. Verfahren nach Anspruch 21, in dem das kationische oberflächenaktive Mittel aus der Gruppe ausgewählt ist, bestehend aus ein-, zwei- und dreiwertigen Alkylaminen, ethoxylierten Aminen, quartären Ammoniumverbindungen und Ampholyten ausgewählt ist.

23. Verfahren nach Anspruch 22, in dem das kationische oberflächenaktive Mittel ein Imidazolinderivat, wie 1-(2-Hydroxyethyl)-2-C<sub>8-22</sub>-alkyl- oder -C<sub>8-22</sub>-Alkenyl-2-imidazolin, ist.

24. Verfahren nach einem der Ansprüche 1 bis 23, in dem die Emulsion ferner Stabilisatoren, Gefrierschutzmittel, Korrosionsinhibitoren und Hydrophobizität verleihende Mittel enthält.

25. Verfahren nach Anspruch 24, in dem die Emulsion ferner ein oder mehrere Glykole und/oder Glykolether und/oder Polyglykole, in denen die Anzahl der Ethergruppen 5 nicht übersteigt, und/oder Glycerin in einer Menge von 1 bis 20 Gew% der gesamten Emulsion enthält.

26. Verfahren nach einem der Ansprüche 1 bis 24, in dem die Emulsion eine Viskosität von höchstens 40 cP, gemessen bei 40 °C mit einem Emila-Viskosimeter, aufweist.

27. Verfahren nach einem der Ansprüche 1 bis 26, in dem die Emulsion ferner ein anionisches oberflächenaktives Mittel enthält, das aus der Gruppe ausgewählt ist, bestehend aus C<sub>8-22</sub>-Alkyl- oder C<sub>8-22</sub>-Alkenylsarcosinen, C<sub>6-20</sub>-Alkyl- oder C<sub>6-20</sub>-Alkenylbernsteinsäuren, C<sub>6-20</sub>-Alkyl- oder C<sub>6-20</sub>-Alkenylphenoxyessigsäure, C<sub>8-22</sub>-Alkylsulfamidocarbonsäure, C<sub>1-10</sub>-Alkylarylsulfamidocarbonsäure und Arylsulfamidocarbonsäure, wobei die Gesamtmenge des anionischen oberflächenaktiven Mittels 0,5 bis 12 Gew% und die Menge des kationischen oberflächenaktiven Mittels 5 bis 150 %, berechnet auf der Grundlage der molaren Menge des in der Emulsion vorliegenden anionischen oberflächenaktiven Mittels, beträgt.

28. Verfahren nach einem der Ansprüche 1 bis 27, in dem der pH-Wert der Emulsion 7,4 bis 10,5, vorzugsweise 7,8 bis 10, insbesondere 8,2 bis 9,5, beträgt.

29. Verfahren nach einem der Ansprüche 1 bis 28, in dem die Emulsion in einer Menge von 10 bis 100 g/m<sup>2</sup>, insbesondere 20 bis 50 g/m<sup>2</sup>, auf die Form aufgebracht wird.

30. Verfahren zum Verbessern der Freigabe eines geformten Betonkörpers aus der Form durch Aufbringen einer wirksamen Menge einer Öl-in-Wasser-Emulsion, hergestellt durch Zugabe von Wasser zu einem Emulsionskonzentrat, wie es in einem der Ansprüche 1 bis 28 definiert ist und das kein Wasser enthält.

#### Revendications

1. Un procédé pour améliorer l'enlèvement du moule d'un article en béton moulé en appliquant au moule une quantité efficace d'une composition de démoulage du béton, cette composition étant une émulsion du type huile dans l'eau contenant de l'eau à raison de 10-90 % du poids de l'émulsion totale, un constituant huileux à raison de 10-90 % du poids de l'émulsion totale, un ou plusieurs agents tensio-actifs non-ioniques à raison de 0,5-20 % du poids de l'émulsion totale et un ou plusieurs agents tensio-actifs anioniques présents sous la forme d'un sel de sodium, de potassium, de lithium, d'ammonium ou d'un sel d'une alcoylamine inférieure, d'une alcoyl-alcanolamine inférieure ou d'un sel d'alcanolamine inférieure d'au maximum 8 atomes de carbone ou d'un sel mixte, la quantité de l'agent tensio-actif anionique par rapport à l'agent tensio-actif non-ionique étant de 1-100 % en poids et sous réserve que la somme des ingrédients dans la composition n'excède pas 100 %.

2. Un procédé selon la revendication 1, dans lequel le constituant huileux est une huile minérale.
3. Un procédé selon la revendication 2, dans lequel l'huile minérale comprend au maximum 9 % de composés aromatiques.
- 5 4. Un procédé selon la revendication 2, dans lequel l'huile minérale a un point d'ébullition d'au moins 250°C.
5. Un procédé selon la revendication 1, dans lequel le constituant huileux est un triglycéride ayant 10-24 atomes de carbone dans chaque portion acide gras, éventuellement en mélange avec une huile minérale.
- 10 6. Un procédé selon la revendication 5, dans lequel le rapport entre l'huile minérale et le triglycéride ayant 10-24 atomes de carbone dans chaque portion acide gras est compris entre 99:1 et 50:50.
7. Un procédé selon la revendication 1, dans lequel le constituant huileux comprend un ester d'un acide carboxylique aliphatique avec un alcool mono- ou dihydrique, le nombre total d'atomes de carbone dans les esters étant de 8-46, et ayant un point de fusion d'au maximum 35°C.
- 15 8. Un procédé selon la revendication 1, dans lequel l'ester constitue de 1 à 100 % du constituant huileux, la partie restante étant de l'huile minérale et/ou un triglycéride ayant 10-24 atomes de carbone dans chaque portion acide gras.
- 20 9. Un procédé selon l'une quelconque des revendications 1-8, dans lequel la teneur en constituant huileux est de 15-65 %, de préférence 25-55 %, en poids par rapport à l'émulsion totale.
- 25 10. Un procédé selon l'une quelconque des revendications 1-9, dans lequel la quantité de l'agent tensio-actif anionique, calculée en poids par rapport à la quantité de l'agent tensio-actif non-ionique est de 2-50 %, spécialement 4-25 %.
- 30 11. Un procédé selon l'une quelconque des revendications 1-9, dans lequel la quantité d'agent tensio-actif anionique est de 0,05-6 % en poids, de préférence 0,1-4 %, en particulier 0,15-2 % et spécialement 0,2-1 % en poids par rapport à l'émulsion totale.
- 35 12. Un procédé selon l'une quelconque des revendications 1-11, dans lequel l'agent tensio-actif anionique est un sel d'un ester d'acide mono- ou diphosphorique d'un C<sub>4-15</sub> alcoylphénol éthoxylé, d'un di-C<sub>2-15</sub> alcoylphénol éthoxylé ou d'un alcool gras en C<sub>3-22</sub> éthoxylé.
- 40 13. Un procédé selon l'une quelconque des revendications 1-11, dans lequel l'agent tensio-actif anionique est choisi dans le groupe constitué par les sels de C<sub>8-22</sub> alcoylsarcosines, d'acides C<sub>1-15</sub> alcoylphénylcarboxyliques, d'acides arylcarboxyliques d'acides aryl-C<sub>1-15</sub> alcoylcarboxyliques, d'acides C<sub>1-15</sub> alcoylaryl-C<sub>1-15</sub> alcoylcarboxyliques, d'acides phénoxy-C<sub>1-15</sub> alcoylcarboxyliques, d'acides C<sub>1-15</sub> alcoylphénoxy-C<sub>1-15</sub> alcoylcarboxyliques, d'acides C<sub>8-30</sub> alcoylcarboxyliques et des acides dicarboxyliques correspondants et de leurs analogues correspondants insaturés et les sels d'acides insaturés dimérisés ou trimérisés.
- 45 14. Un procédé selon la revendication 10 ou 11, dans lequel l'agent tensio-actif anionique est un sel d'un acide en C<sub>12-30</sub> saturé tel que les acides laurique, myristique, palmitique et stéarique.
15. Un procédé selon l'une quelconque des revendications 1-14, dans lequel la quantité de l'agent ou des agents tensio-actifs non-ioniques est de 1-12 % en poids par rapport à l'émulsion totale, de préférence 2-7 % en poids.
- 50 16. Un procédé selon la revendication 15, dans lequel l'agent ou les agents tensio-actifs non-ioniques sont choisis parmi des agents tensio-actifs éthoxylés, propoxylés ou co-éthoxylés/propoxylés ayant un équilibre hydrophile-lipophile correspondant à une valeur de HLB comprise entre 5,0 et 11.
17. Un procédé selon la revendication 16, dans lequel la valeur de HLB est comprise entre 5,5 et 9,9, de préférence entre 6,0 et 9,0.
- 55 18. Un procédé selon les revendications 1-15, dans lequel la composition des agents tensio-actifs non-ioniques comprend au moins un membre du groupe constitué par les agents tensio-actifs tels que définis dans les revendica-

tions 16 ou 17, les monoglycérides d'acides gras en  $C_{8-24}$  saturés et insaturés, portant éventuellement un groupe hydroxy, et les monoglycérides mono- ou di-( $C_{1-4}$ )-acylés d'acides gras en  $C_{2-24}$ , portant éventuellement un groupe hydroxy.

- 5 19. Un procédé selon l'une quelconque des revendications 1-15, dans lequel la composition des agents tensio-actifs non-ioniques comprend un monoglycéride mono-ou di-( $C_{1-4}$ )-acylé d'acides gras en  $C_{2-24}$ , portant éventuellement un groupe hydroxy, et éventuellement un ou plusieurs agents tensio-actifs tels que définis dans la revendication 16 et/ou un ou plusieurs monoglycérides d'acides gras en  $C_{8-24}$  saturés ou insaturés, portant éventuellement un groupe hydroxy.
- 10 20. Un procédé selon l'une quelconque des revendications 16-19, dans lequel l'agent ou les agents tensio-actifs éthoxylés sont choisis dans le groupe constitué par le nonylphénol éthoxylé, le dinonylphénol éthoxylé, des alcools gras en  $C_{8-22}$  éthoxylés et des esters de polyéthylèneglycol d'acides gras en  $C_{10-22}$ .
- 15 21. Un procédé selon l'une quelconque des revendications 1-20, dans lequel l'émulsion comprend en outre un agent tensio-actif cationique ayant au moins 10 atomes de carbone dans la partie hydrophobe de la molécule, à raison de 5-100 % par rapport à la quantité molaire de l'agent tensio-actif anionique.
- 20 22. Un procédé selon la revendication 21, dans lequel l'agent tensio-actif cationique est choisi dans le groupe constitué par des alcoylamines mono-, di- et trivalentes, des amines éthoxylées, des composés d'ammonium quaternaire et des ampholytes.
- 25 23. Un procédé selon la revendication 22, dans lequel l'agent tensio-actif cationique est un dérivé d'imidazoline tel qu'une 1-(2-hydroxyéthyl)-2- $C_{8-22}$  alcoyl ou - $C_{8-22}$  alcényl-2-imidazoline.
- 30 24. Un procédé selon l'une quelconque des revendications 1-23, dans lequel l'émulsion comprend aussi des stabilisants, des antigels, des inhibiteurs de corrosion et des agents donnant le caractère hydrophobe.
- 35 25. Un procédé selon la revendication 24, dans lequel l'émulsion comprend en outre un ou plusieurs glycols et/ou glycol éthers et/ou polyglycols dans lesquels le nombre de groupes éther ne dépasse pas 5 et/ou du glycérol à raison de 1-20 % en poids par rapport à l'émulsion totale.
- 40 26. Un procédé selon l'une quelconque des revendications 1-24, dans lequel l'émulsion a une viscosité d'au maximum 40 cPo quand elle est mesurée à 40°C sur un viscosimètre Emila.
- 45 27. Un procédé selon l'une quelconque des revendications 1-26, dans lequel l'émulsion comprend en outre un agent tensio-actif anionique choisi dans le groupe constitué par les  $C_{8-22}$  alcoyl ou  $C_{8-22}$  alcényl sarcosines, les acides  $C_{6-20}$  alcoyl ou  $C_{6-20}$  alcényl succiniques, les acides  $C_{6-20}$  alcoyl ou  $C_{6-20}$  alcénylphénoxyacétiques, les acides  $C_{8-22}$  alcoylsulfamido carboxyliques, les acides  $C_{1-10}$  alcoylaryl-sulfamido carboxyliques et les acides arylsulfamido carboxyliques, la quantité totale d'agent tensio-actif anionique étant de 0,5-12 % en poids et la quantité totale de l'agent tensio-actif cationique étant de 5-150 %, en calculant par rapport à la quantité molaire de l'agent tensio-actif anionique présente dans l'émulsion.
- 50 28. Un procédé selon l'une quelconque des revendications 1-27, dans lequel le pH de l'émulsion est de 7,4-10,5, de préférence 7,8-10 et en particulier 8,2-9,5.
- 55 29. Un procédé selon l'une quelconque des revendications 1-28, dans lequel l'émulsion est appliquée au moule à raison de 10-100 g/m<sup>2</sup>, spécialement de 20-50 g/m<sup>2</sup>.
30. Un procédé pour améliorer l'enlèvement du moule d'un article en béton moulé en appliquant une quantité efficace d'une émulsion du type huile dans l'eau préparée par addition d'eau à un concentré pour émulsion tel que défini dans l'une quelconque des revendications 1-28, ne contenant pas d'eau.